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THE EGGERTZ TEST FOR COMBINED CARBON IN STEEL.[1]

By J. H. WHITELEY
(South Durham Steel and Iron Co., Stockton-on-Tees).

INTRODUCTION.

The present Report is a contribution to the study of the problems connected with the colour method devised by Eggertz for the rapid estimation of combined carbon in ordinary steels. This method, in spite of its inaccuracies, is still indispensable in steel-works practice, and although it has been subjected to a great deal of research in the past, some of the problems it offers still remain unsolved. The investigation now to be recorded had three main objects in view—(1) to locate the so-called "missing" carbon; (2) to ascertain more closely than had hitherto been done the relationship between the structure of the carbide in the steel and the result given by the test; (3) to study the reactions which occur, to obtain evidence, if possible, which would indicate the condition of the carbon in quenched steels.

No attempt has been made to determine the constitutional formulæ of the compounds which give rise to the colour, but some of their properties have been closely examined; also, the results obtained by the method have been correlated with the hardness of the steels as given by the Brinell ball test.

The Report has been divided into four parts. In Part I. a description is given of the method used throughout for estimating small amounts of carbon dioxide as barium carbonate. This method possesses several advantages over that in which caustic potash (or a similar reagent) is used as the absorbent, and without it the examination of the nitrous gases for their carbon content could not have been satisfactorily made. Part II. gives a detailed account of the methods used to determine the amount and condition of the carbon in the gases evolved when steel is dissolved

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[1] Carnegie Research Report, received April 11, 1917.

in dilute nitric acid, as in the test. Part III. deals with the nature of the reactions occurring in the solution. In this connection the bearing of the size of the carbide particles in the steel on the results has been closely examined. Part IV. deals chiefly with the correlation of the Eggertz results and the Brinell hardness.

It should be observed here, that throughout the investigation the samples were taken in the form of drillings (or crushed pieces) unless otherwise stated.

PART I.

METHOD FOR THE ESTIMATION OF SMALL AMOUNTS OF CARBON DIOXIDE.

Owing to the difficulties attending the accurate estimation of small amounts of carbon dioxide by absorption in potassium hydrate, the method of absorption in ammoniacal solution of barium chloride, as recommended by McFarlane and Gregory,[1] was adopted in a modified form, and was found to yield very accurate results. It is especially suitable for the examination of the gases given off on dissolving steel samples in nitric acid; since the result is not affected by the acidity of the gases, the complicated apparatus required for the destruction of the nitrous fumes is not necessary.

In using this absorbent, advantage is taken of the fact that on passing carbon dioxide through it at ordinary temperatures soluble barium carbamate is formed which, on heating to 100° C., is converted into the insoluble carbonate. On cooling, this can be filtered off and weighed without any danger of error arising from the presence of carbon dioxide in the air.

The apparatus employed for the estimation of carbon in steel by combustion is shown in Fig. 1, and consists of the following:

A. Gas-holder containing air.

B. Mohr's potash bulb containing a strong solution of potassium hydrate.

C. Bottle with tubulure containing about 1 lb. of moist granulated soda lime.

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[1] *Chemical News*, 1906, vol. 94, p. 133.

D. Thick-walled silica combustion tube, 1 inch internal diameter and about 2 feet 3 inches long, fitted up in the usual way with a plug of copper oxide wrapped in asbestos.

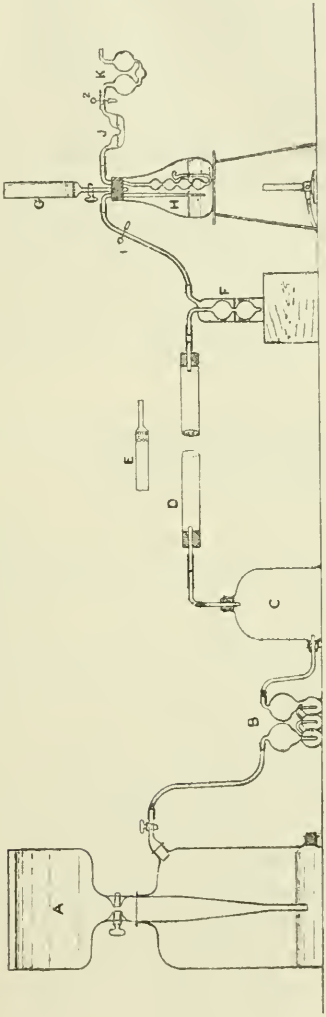

FIG. 1.

F. Arnold's absorption bulb containing a solution of chromic acid and a few drops of sulphuric acid.

H. Conical flask of about 350 cubic centimetres capacity in which the carbon dioxide is absorbed. It is fitted with a rubber stopper through which passes—(1) An inlet tube that reaches to the bottom of the vessel and is narrowed to a moderately fine point, so as to facilitate the absorption of the gas by preventing the formation of very large bubbles. The presence of a little sulphuric acid in bulb F is essential, as it prevents the point of this tube from getting blocked by the precipitate. (2) The filter tube G, which holds a pulp filter supported on a small perforated disc of porcelain; the narrow absorption tube used in Stead's gas apparatus is convenient for this purpose. (3) Exit tube in which four small bulbs are blown; the small bent tube attached to the lower end rises above the liquid in the flask as far as the third bulb, as shown. By means of this device the complete absorption of the carbon dioxide is obtained without the necessity of using a second flask. The small trap, J, is attached to the exit tube.

K. U-tube or trap containing a saturated solution of barium hydrate to prevent any entrance of carbon dioxide from the air. Spring clips 1, 2, are placed as shown.

Either the direct or indirect method of combustion may be employed. In the indirect, a solution of potassium cupric chloride is made in the usual way by dissolving 300 grammes of the salt in 1000 cubic centimetres of distilled water and 65 cubic centimetres of hydrochloric acid, and filtering through an ignited asbestos pulp. 60 cubic centimetres of this solution are used for each gramme of drillings taken for analysis, and the sample is dissolved either in the cold or at a temperature not exceeding 60° C. The carbonaceous residue is collected on an ignited asbestos pulp in a fused silica tube of the Allyn's type shown in Fig. 1, E. After washing, the tube is placed in an air-oven and dried at 100° to 110° C. The asbestos pulp is pushed to one side to allow the free passage of air through the tube and hasten the drying. If the filtrate is kept apart from the washings and re-chlorinated after the addition of 2 cubic centimetres of hydrochloric acid to each 60 cubic centimetres, it can be used for several estimations.

The prepared sample is placed in the combustion tube about 3 inches from the copper oxide. Clip 1 is closed and the apparatus tested for any leakage by applying air pressure from

A. The pulp filter having been made in the tube G, about 100 cubic centimetres of distilled water is placed in flask H, and the cork is tightly fitted in. The flask is then connected with the bulb F, the gas lit below the copper oxide, clip 1 opened, and a steady stream of air allowed to pass through the apparatus. All traces of carbon dioxide are next removed from the flask by boiling the water in it for a few minutes.

In the meantime 20 cubic centimetres of a solution of barium chloride, containing 250 grammes per litre, is mixed with 15 to 20 cubic centimetres of 0·880 ammonia and diluted to 100 cubic centimetres with hot water. The mixture is placed in a beaker and brought to the boil. When this is nearly ready the gas under the flask is turned off, and as soon as the steam pressure will permit clip 2 is closed. The filter tube G is then filled with the boiling barium chloride solution, and on closing clip 1 and opening the stop-cock the liquid is drawn into the flask. The filtration should not be too rapid at first, and can be regulated by opening clip 1 to release excessive pressure. With a little practice there is no difficulty in obtaining a perfectly clear filtrate; the barium chloride solution must, of course, be kept hot while filtering.

Not more than 20 cubic centimetres of ammonia at most should be used; with greater amounts the whole of the carbonic acid present may not be precipitated in the beaker, and on dilution of the solution with the water in the flask more barium carbonate may be thrown down. When the filtration is finished the tap of the filter tube is closed and clip 1 opened. After connecting the bulb K to the apparatus clip 2 is opened. To fill the bulbs of the exit tube and trap J, the flask is tilted until the narrow bent end of the tube dips below the liquid. The air pressure forces the liquid into the bulbs of the exit tube, and when the top bulb is full the flask is tilted in the opposite direction so as to allow a little of the solution to enter the trap J. Excess of liquid can be withdrawn from the exit tube by closing clip 1 and slightly cooling the air in the flask.

If the combustion is to be made with cylinder oxygen this is now turned on, and must be replaced by air as soon as the sample is burnt off. After a short while the gas is lighted under the sample. The barium chloride solution is best kept fairly hot during the absorption ; it should remain perfectly clear until the carbonic acid from the sample enters the flask. During the process the solution in trap J should occasionally be brought to the boil with a small spirit flame. The formation of any trace of precipitate in it is a certain indication that the rate of flow of the gases into the apparatus is too fast ; a clear liquid shows that complete absorption is taking place in the flask and tube.

When the absorption is completed clip 1 is closed, trap K is removed, and the liquid in the exit tube bulbs is drawn into the flask. The barium chloride solution is then brought to the boil, and after boiling gently for about half a minute the gas is turned off ; as soon as the steam pressure will allow, clip 2 is closed and clip 1 opened. The solution can then be rapidly cooled to 15° C.

The precipitate is filtered as quickly as possible through an ashless pulp filter and the flask and exit tube are well rinsed out. The pulp should be washed several times before air is allowed to pass through it. The small amount of precipitate which adheres to the flask is easily removed with a rod.

In washing, wash bottles should not be used. A glass jet connected by a long piece of rubber tubing with a tank of distilled water placed about 3 feet above the bench is quite satisfactory for the purpose. The flow of water can be regulated with a pinch-cock held just behind the jet.

The thoroughly washed pulp and precipitate are finally placed in a platinum capsule and ignited either in a muffle furnace at a temperature not exceeding 900° C., or on a pipeclay triangle over a Meker burner.

The percentage of carbon is found by multiplying the weight of barium carbonate obtained from 1 gramme of sample by 6·09. The precipitate occludes a little barium chloride, but the amount is so small as to be negligible.

Starting with clear absorption solutions, blank tests when made with porcelain or non-porous silica tubes do not exceed 0·004 gramme. By passing the air through a heated tube before it enters the purifying train the amount of " blank " can be reduced to about 0·002 gramme.

The method can readily be tested by heating weighed amounts of pure dry calcium carbonate (0·05 to 0·15 gramme) in the combustion tube in a current of purified air and absorbing the expelled carbonic acid.

It is important to note that the weight of precipitate in an estimation must not exceed 0·30 gramme; with larger amounts a complete precipitation may not be obtained in the flask on boiling. The weight of sample taken for analysis must be regulated, therefore, so as to avoid error from this source.

TABLE I.—*Particulars of Samples used in the Experiments.*[1]

Sample.	Description.	Carbon per Cent. by Combustion.	Carbon per Cent. by Colour. Drillings Used.	Manganese per Cent.
A	Cut from a large slab 8 inches thick rolled from the lower end of a 5-ton ingot.	0·17	0·17	0·51
B	Drillings from a bath sample taken from same charge as sample F.	0·27	0·29	0·02
C	Annealed test-piece of cast steel.	0·28	0·285	0·44
D	Drillings from a bath sample (acid steel).	0·31	0·305	0·01
E	Taken from a large annealed casting, in which the cementite had completely balled up.	0·37	0·42	0·49
F	Pit sample from an acid steel charge.	0·38	0·375	0·81
G	3-inch round (basic steel), as rolled .	0·42	0·42	0·64
H	Large bath sample of acid steel forged into a bar ¾ inch square.	0·50	0·52	0·02
J	Basic steel round 1¼ inch diameter, as rolled.	0·54	0·54	0·95
K	Drillings from acid steel bath sample.	0·55	0·57	0·02
L	Basic steel rail, as rolled.	0·56	0·56	0·71
M	Small steel plate ⅜ inch thick, as rolled.	0·71	0·66	1·30
N	Basic steel flat 2 inches thick 9 inches wide. This sample was taken as standard in estimating the colour-carbons.	0·78	...	0·75
P	Piece taken from a steel roll (outer portion).	0·84	0·86	0·79
R	Bar of ordinary tool steel 1½ inch square annealed at 650° C. for two hours.	1·39	1·41	0·40
S	Bar of ordinary hard steel used for wire drawing.	2·35	2·45	0·61

The addition of 0·1 gramme of ammonium chloride or nitrate to the solution before filtering into the flask was found to have no effect upon the result, a confirmation of the statement of

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[1] No sample contained over 0·06 per cent. of sulphur or phosphorus, and each sample was practically uniform in composition.

McFarlane and Gregory[1] that the effect of chloride formed in the reaction was negligible.

The combustion values and other data for the samples used in the experiments described in this Report are collected in the table on p. 7.

PART II.

THE ESTIMATION OF THE CARBON COMPOUNDS CONTAINED IN THE GASES GIVEN OFF IN THE EGGERTZ TEST.

I. Preliminary Tests.

The initial experiments were made by dissolving the steel samples in dilute nitric acid and passing the liberated gases over red-hot copper oxide, after washing them in strong solutions of ferrous sulphate to remove the greater part of the nitrous fumes. The carbonic acid obtained was absorbed and estimated as described in Part I. In this way the total amount of the carbon evolved as carbonic acid, carbon monoxide, and hydrocarbons (insoluble in ferrous sulphate solution) was determined.

The arrangement of apparatus used for the purpose is shown in Fig. 2.

Description of Apparatus.—A, B. Specially designed glass vessel in which the samples were dissolved. The capacity of the upper bulb, A, was about 50 cubic centimetres, and that of the lower, B, 60 to 70 cubic centimetres. The inlet tube was drawn to a fine point and passed through a tightly fitting piece of rubber tubing which connected it with the tubulure in the lower bulb. Both the upper bulb and the inlet tube were connected with the air-purifying train through the T-piece.

C. Porcelain basin containing water in which B was placed.

D, E. Absorption vessels containing fresh strong solutions of ferrous sulphate in water. E was connected with the combustion tube by means of a bent piece of glass tubing.

F. Absorption bulb holding a saturated solution of pure potassium permanganate which served to absorb most of the nitrous fumes that had escaped absorption by the ferrous sulphate solutions.

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[1] *Loc. cit.*

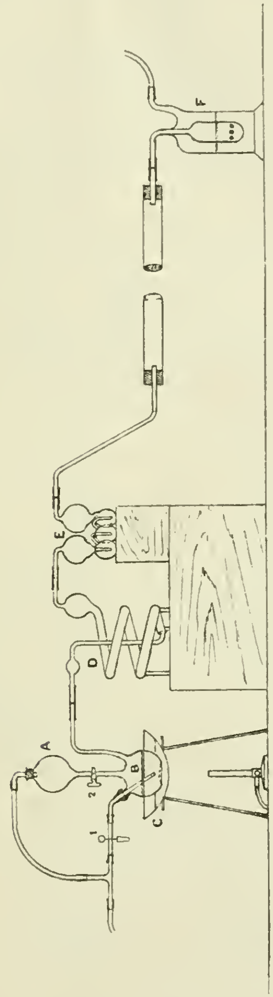

Fig. 2.

(Shown in Fig. 1.) Absorption flask and trap containing the ammoniacal solution of barium chloride (H, J).

The acid fumes which are evolved readily attack rubber and cause carbonaceous gases to be liberated ; the connections were made, therefore, with pieces of rubber tubing in such a way that as little as possible was exposed to the gases. The first rubber bung in the combustion tube was gradually corroded in this manner, but the amount of carbon given off from it in each estimation was found to be small and constant, and was included, of course, in the blank tests which were occasionally made.

Method of Analysis.—One gramme of the sample having been placed in B, 20 cubic centimetres of nitric acid (1·12 sp. gr.) was poured into the upper bulb A. The apparatus was connected up as shown in Fig. 2 and tested for leakages, and purified air was then passed slowly through it. After having prepared a clear solution of ammoniacal barium chloride in the flask, as described in Part I., and heated up the copper oxide in the combustion tube, clip 1 was closed and stop-cock 2 opened and the nitric acid was forced into B gradually, especially when using fine drillings. As soon as the reaction in B had subsided, clip 1 was opened and a slow current of air was again passed through. The volume of D and E was sufficient to prevent the initial gases rushing past the hot copper oxide too rapidly. In these experiments the inlet tube was kept above the liquid in B. The water in C was next quickly brought to the boil and boiled for exactly ten minutes, after which the vessel B was cooled by replacing the tripod and basin C with another tripod and basin containing cold water. Air was allowed to pass through the apparatus for about fifteen minutes longer, and finally the barium chloride solution was boiled and the carbonate filtered off and weighed.

The blank tests were made by using a sample of iron containing only a trace of carbon. They consistently gave 0·006 gramme of barium carbonate. Weighed portions of pure calcium carbonate (0·02 to 0·03 gramme) were added to some of the blank tests, and dissolved along with the iron. In each instance the full amount of precipitate was obtained. In order to test the effect on the absorption of the presence of acid fumes in the gases entering the flask, some strong nitric acid was placed in F, and the carbonic acid from the ignition in the combustion tube of a weighed quantity of calcium carbonate was absorbed and weighed. As the correct amount of barium carbonate was obtained, it was concluded that in the experiments on steel samples any acid fumes which might enter the flask could not interfere with the accuracy of the results. Since the gases from the samples were passed over hot copper oxide, all hydrocarbons and carbon monoxide present would be oxidised to carbonic acid. This was shown to be the case by mixing 15 cubic centimetres of coal gas with about 200 cubic centimetres of the gases given off on dissolving pure iron in nitric acid and passing the mixture over the heated oxide. The bulky precipitate of barium carbonate which came down in the absorption flask was found, on weighing, to contain approximately the same amount of carbon as that present in the coal gas used.

TABLE II.—*Results of Preliminary Tests* (*ten minutes' heating at* 100° *C.*).

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. Evolved.	Percentage of Total Carbon in the Gases.
A	Normal[1]	0·17	0·037	22·0
C	,,	0·28	0·072	25·5
D	,,	0·31	0·072	23·0
,,	Quenched	0·31	0·069	22·0
E	Normal	0·37	0·090	24·0
F	,,	0·38	0·095	25·0
,,	Quenched	0·38	0·092	24·0
H	Normal	0·50	0·110	22·0
L	,,	0·56	0·130	23·0
M	,,	0·71	0·150	21·0
N	,,	0·78	0·185	23·5
,,	Quenched	0 78	0·190	24·0
R	Normal	1·39	0·315	22·5
,,	Quenched	1·39	0·300	21·5

A second series of similar tests was made in which the samples, after dissolving, were heated for five minutes only at 70° C.

TABLE III.—*Results of Preliminary Tests* (*five minutes' heating at* 70° *C.*).

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. Evolved.	Percentage of Total Carbon in the Gases.
A	Normal	0·17	0·018	10·5
E	,,	0·37	0·037	10·0
G	,,	0·42	0·038	9·0
N	,,	0·78	0·074	9·5
,,	Quenched	0·78	0·074	9·5
R	Normal	1·39	0·144	10·0

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[1] The word "normal" is used throughout to indicate the original condition of the sample as described in Table I.

A third series of experiments was also made in which the gases were not passed over heated copper oxide. In every other detail the tests were made in precisely the same way as those of the first series (Table II.). The results (Table IV.) indicate, therefore, the amount of carbon which is liberated as carbonic acid in ten minutes' heating at 100° C. Blank tests did not exceed 0·004 gramme.

TABLE IV.—*Results of Preliminary Tests for CO_2 only (ten minutes' heating at* 100° *C.).*

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. Evolved as CO_2.	Percentage of Total Carbon Evolved as CO_2.
E	Normal	0·37	0·08	21·5
F	,,	0·38	0·09	23·0
,,	Quenched	0·38	0·09	23·0
M	Normal	0·71	0·150	21·0
N	,,	0·78	0·165	21·0
,,	Quenched	0·78	0·162	21·0
,,[1]	Normal	0·78	0·185	23·5
R	,,	1·39	0·295	21·0

It is clearly evident on comparison of Tables II. and IV. that the carbon contained in the gases, after they have been washed in the ferrous sulphate solutions, is almost entirely in the form of carbonic acid, in both quenched and normal samples; also, the ratio of the carbon evolved to the amount present in the samples is practically constant. All the quenched steels employed gave less than 60 per cent. of the true carbon value when tested by colour against a normal standard. The conclusion arrived at by Osmond and Werth[2] as a result of their experiments, that the "missing" carbon was to be found in the washed evolved gases, has therefore not been confirmed.

II. THE AMOUNT OF CARBON DIOXIDE GIVEN OFF ON FURTHER HEATING.

The next series of experiments was made in order to find the amount of carbon dioxide given off when the period of boiling was increased to forty minutes. In these tests, the vessel A, B (Fig. 2), containing 1 gramme of sample, was connected directly with the absorption flask, which was placed in the position occupied by D (Fig. 2). After the clear barium chloride solution had been prepared, the flask was disconnected from A, B, and temporarily joined to the air-purifying train by means of the rubber tubing attached to the upper bulb. Clip 2 (Fig. 1) was kept closed. Clip 1 (Fig. 2) was closed until the drillings in B had been dissolved in 20 cubic centimetres of dilute nitric acid (1·12 sp. gr.). Clip 1 was then opened and the water in C brought to the boil and boiled for ten minutes. The gases given off during this period were allowed to escape into the air. The connection between A, B, and the absorption flask was made again, clip 2 (Fig. 1) opened, and the inlet tube was lowered below the liquid in B. The heating was now continued for thirty minutes longer, during which time a very slow current of air was continuously passed through the apparatus. It was found that during the first ten minutes' boil, after dissolving, the carbon dioxide formed in the solution was removed by the other gases liberated, and so, in order to reproduce as far as possible the conditions of the Eggertz test, air was not bubbled through the solution in B in the preliminary tests; when heating thirty minutes longer, however, this was necessary. The blank tests which were made gave 0·002 gramme of precipitate.

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[1] 10 cubic centimetres extra of strong nitric acid added after dissolving.

[2] *Mémorial de l'artillerie de la Marine*, 1887.

TABLE V.—*Carbon Dioxide evolved on Heating during the Period Ten to Forty Minutes.*

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. Evolved as CO_2.	Percentage of Total Carbon Evolved as CO_2.
A	Normal	0·17	0·018	10·5
C	,,	0·28	0·03	10·5
F	,,	0·38	0·04	10·5
,,	Quenched	0·38	0·04	10·5
L	Normal	0·56	0·06	10·5
N	,,	0·78	0·075	9·5
,,	Quenched	0·78	0·075	9·5

Two similar experiments were next made on sample N, in the normal and quenched states, in which the boiling was continued from ten minutes to four hours. One gramme portions were again used, and an extremely slow current of air employed. The results were identical, 0·17 per cent. of carbon being obtained from each. The amount of carbonic acid liberated on boiling for a still longer time was too small to determine accurately on these samples. In order to complete the investigation, therefore, 3 grammes of sample S were dissolved in 60 cubic centimetres of dilute nitric acid and boiled in a reflux boiling flask for five hours. The solution was then transferred to the apparatus and the amount of carbonic acid liberated in the sixth hour's boil was estimated. It was found that 0·027 per cent. of carbon had been given off in this period.

On consideration of these and the previous results, it is at once evident that the quantity of carbon dioxide evolved in the Eggertz test from either quenched or normal steels is greatest in the first few minutes and rapidly falls as the heating is continued. To obtain an approximate idea of the change in speed of this reaction, the average amount of carbon given off in each ten minutes of the different periods of boiling from a sample containing 1 per cent. has been calculated and is given in the following table:

TABLE VI.—*Carbon Dioxide evolved from a Normal or Quenched Steel containing* 1 *per cent. Carbon.*

Period of Boiling.	Average Carbon per Cent. Evolved in each 10 Minutes as CO_2.	Percentage of Total Carbon Evolved in each Period as CO_2.
10 min.	0·21	21·0
10 to 40 min.	0·032	9·6
40 min. to 4 hours	0·006	12·0
5 hours to 6 hours	0·0019	1·1

III. THE EXAMINATION OF THE FILTRATE AND PRECIPITATE SEPARATELY.

A few experiments were made in which the solution and precipitate formed on dissolving a normal steel at about 50° C. were examined separately for the amounts of carbon dioxide liberated on heating. One gramme portions were dissolved and filtered. The filtrates were then transferred to the vessel B

(Fig. 2) and the carbon dioxide given off during the first ten minutes' boil was estimated. Most of the brown precipitate from each sample was washed from the filter paper with 20 cubic centimetres of dilute nitric acid in which 1 gramme of pure iron had been dissolved. The acid (and precipitate) was then treated in the same manner as the filtrates. In another experiment the precipitate was boiled in dilute nitric acid (1·2) only.

The results showed that the carbon dioxide was liberated from both filtrate and precipitate, and that the reaction was not influenced by the presence of the iron.

TABLE VII.—*Results of the Separate Treatment of Filtrate and Precipitate.*

Sample.	Carbon per Cent. evolved as CO_2 in Ten Minutes.			
	Preliminary Test (Table II.).	Filtrate only.	Precipitate only, with Iron.	Precipitate, without Iron.
M	0·150	0·062	0·08	...
N	0·185	0·080	0·08	0·08

IV. THE ESTIMATION OF COMBINED CARBON IN STEEL: A SUGGESTED NEW METHOD.

Seeing that the ratio between the carbon evolved as carbon dioxide and the amount present in the sample was practically constant throughout, experiments were made to ascertain whether advantage could be taken of this reaction for the purpose of estimating the combined carbon in steel. Preliminary tests were made with standard samples, high in carbon, to find the weight of sample required in order that the amount of barium carbonate obtained, during a twenty minutes' boil, should represent one-tenth of the percentage of the carbon in the steel. As by far the greater bulk of the carbon dioxide is evolved in the first twenty minutes' heating, this period was chosen as the most suitable for the purpose. After a number of experiments, 2·45 grammes of the sample were found to yield the quantity of barium carbonate required.

The apparatus employed is shown in Fig. 3. The Mohr's bulb D contains about 10 cubic centimetres of a solution of potassium permanganate made by dissolving 50 grammes of the salt in 500 cubic centimetres of water containing 50 cubic centimetres of dilute sulphuric acid (1–3 aq. by vol.), and boiling for a few minutes. This solution is used to absorb most of the acid fumes which are given off in the process. After having rinsed out the bulbs A, B, with hot water, 2·45 grammes of clean drillings are placed in B and 50 cubic centimetres of dilute nitric acid (1·2 sp. gr.) in A. The inlet tube is next inserted, and the vessel is connected with the air-purifying train and the Mohr's bulb in the manner shown in Fig. 3. When all the connections have been found to be air-tight, a clear solution of ammoniacal barium chloride is prepared in the absorption flask H and trap J, as previously described. The basin C is now filled with cold water, clip 1 is closed and stop-cock 2 opened, and the nitric acid is forced into B a little at a time until the whole has been introduced. The initial gases from steels when dissolved in the cold do not contain any carbon dioxide, so that, if the sample is dissolved gradually and kept cool, any danger of loss from incomplete absorption owing to the rapid evolution of the initial gases is avoided. The water in C is now quickly brought to the boil. Clip 1 is opened again and

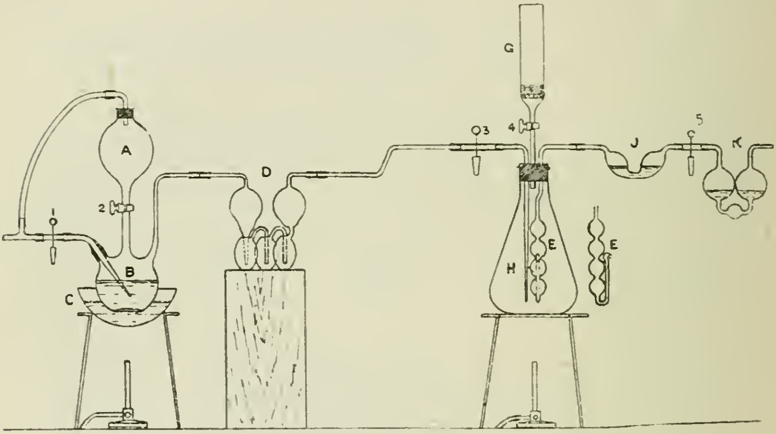

Fig. 3.

a very slow current of air allowed to pass through the apparatus. After the water has boiled for exactly twenty minutes the tripod and basin C are replaced by another tripod and basin containing cold water, and a quicker current of air is passed through for a few minutes more. The barium chloride solution is next boiled gently for a few seconds and cooled, and the precipitate of barium carbonate filtered off, ignited, and weighed (see Part I.).

Blank tests, when made with pure iron, give a constant amount of 0·003 gramme of barium carbonate provided that the least possible amount of rubber is exposed to the gases. This figure is deducted from the total weight obtained in an estimation, and the percentage of carbon in the sample is found by multiplying the remainder by ten.

An estimation by this method can be made in a little over one hour. It will be seen, on reference to Table VIII., that, with either pearlitic, sorbitic, or martensitic samples, the results provide a useful check on those obtained by combustion.

TABLE VIII.—*Results obtained by the suggested New Method for Carbon.*

Sample.	Carbon per Cent. by Combustion.	Condition of Sample.	Weight of $BaCO_3$ from 2·45 Grammes.
			Gramme.
A	0·17	Pearlitic (photo. 3)	0·0165
E	0·37	Divorced cementite (photo. 6)	0·037
F	0·38	Sorbitic	0·038
J	0·54	Pearlitic (photo. 18)	0·054
,,	0·54	Sorbitic	0·052
,,	0·54	Martensitic	0·053
L	0·56	Pearlitic	0·057
M	0·71	Martensitic	0·070
N	0·78	Divorced cementite	0·078
,,	0·78	Pearlitic (photo. 1)	0·078
,,	0·78	Sorbitic	0·076
,,	0·78	Martensitic	0·077
R	1·39	Massive carbide and "granular pearlite" (photo. 5)	0·140
S	2·35	,, ,,	0·233

V. TESTS ON AUSTENITIC STEEL FOR CO_2 EVOLVED.

Very careful tests were next made on samples of austenite. A bar was cut, about 6 inches long and ¾ inch square section, from sample R (combined carbon, 1·39 per cent.). Drillings were taken 2 inches from each end, and the bar was then cut into five equal parts. These were heat-treated as follows:

A and D were quickly heated to 1150° C. and quenched in iced brine.
B was ,, ,, 750° C. ,, water.
C ,, ,, ,, 1000° C. ,, iced brine.
E ,, ,, ,, 900° C. ,, water.

The typical austenitic structure of specimens A, C, and D is shown in photos. 21 and 22. Sample B contained some troostite and sample E consisted of a mixture of martensite and cementite. These samples were crushed in a hard steel mortar, and the amount of carbon dioxide liberated from 2·45 gramme portions, taken from the interior of each (to avoid error arising from oxidation of the skin), was estimated as described in Section IV.

TABLE IX.—*Carbon Dioxide evolved from Austenitic Steel in Twenty Minutes' Boiling.*

Sample R.	$BaCO_3$ obtained from 2·45 Grammes.	Carbon per Cent given off as CO_2.
	Gramme.	
Drillings (1) taken between A and B	0·140	0·348
,, (2) ,, D and E	0·140	0·348
Specimen A. Austenite . . .	0·132	0·328
,, B. Troostitic . . .	0·141	0·350
,, C. Austenite . . .	0·129	0·321
,, D. ,, . . .	0·131	0·326
,, E. Martensitic . .	0·136	0·339

The solutions were examined carefully for graphite, but no trace could be found in any of them. It was concluded, therefore, that the amount of carbon dioxide liberated from a steel in the austenitic state is slightly lower than the quantity obtained from the same steel in other conditions.[1]

VI. ESTIMATION OF THE AMOUNT OF HYDROCYANIC ACID GIVEN OFF.

It was repeatedly noticed that the permanganate solutions from the Mohr's bulb used in the previous experiments smelled strongly of hydrocyanic acid after the gases from a high carbon steel had passed through them. On filtering off the precipitated manganese oxide and applying the Prussian blue test to the filtrate the characteristic blue colour due to hydrocyanic acid was obtained. The presence of this acid in the gases given off in the Eggertz test appears to have been first noted by Osmond and Werth,[1] who state that 0·05 per cent. of the carbon is evolved in this form.

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[1] This may possibly be due to the presence in the solution of gelatinous pieces of precipitate which dissolve with great difficulty. Since the above was written, it has been found that certain tempered steels (Part IV.) also give this type of precipitate, and such samples may also give low results.

As the Prussian blue test is not quantitative, it was decided to ascertain the amount of hydrocyanic acid in the gases by absorption in caustic potash and titration with a standard solution of silver nitrate. The procedure was as follows:

2·5 grammes of sample were placed in the vessel A, B, (Fig. 2), and the gases formed on dissolving this amount in 50 cubic centimetres of nitric acid (1·2 sp. gr.) were passed through 20 cubic centimetres of a solution of potassium hydrate contained in the Winkler's apparatus D, and 15 cubic centimetres in the Mohr's bulb E (Fig. 2). The caustic potash solution was prepared by dissolving 200 grammes in 1 litre of water. After a number of experiments had been made in this way the Mohr's bulb was discarded, as it was found that the whole of the hydrocyanic acid was retained by the potash contained in the Winkler's apparatus.

The solution of the sample was heated at 100° C. for varying periods of time, during which a steady current of air was passed through the apparatus. The alkaline solution was then transferred to a small beaker and diluted to 60 cubic centimetres; a crystal of potassium iodide was added, and the titration made with a standard solution of silver nitrate. The end point was indicated by the formation of a slight permanent turbidity. The silver solution contained 1 gramme of the salt per litre, and was standardised by adding known quantities of potassium cyanide to 20 cubic centimetres of the caustic potash solution, diluting to 60 cubic centimetres and titrating. Blank tests made with 2·5 grammes of pure iron required 0·4 cubic centimetres. It was found that the presence of nitrite in the potash due to the absorption of nitrogen peroxide did not affect the accuracy of the method.

Some preliminary experiments were made with sample X to find out whether the quantity of hydrocyanic acid liberated in a given time was constant. Both the temperature at which the steel was dissolved and the subsequent rate of flow of the air-current were varied. In order to avoid a very violent reaction when dissolving at 100° C., a single piece of the steel, cut and filed to correct weight, was used.

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[1] *Loc. cit.*

The results of these tests are given in Table X. They show clearly that the amount of the acid given off varies considerably under different conditions. This conclusion was confirmed by adding small quantities of potassium cyanide (0·01 to 0·02 gramme) to 2·5 gramme portions of pure iron after they had been dissolved in the apparatus, and varying the rate of flow of the air. Here, also, the results were erratic, and in no instance did the amount of hydrocyanic acid obtained after one hour's heating exceed 80 per cent. of that added. It was also shown by similar experiments that the acid was liberated gradually, about 50 per cent. usually being obtained in the first ten minutes both from cyanide solutions and steel samples.

TABLE X.—*The Hydrocyanic Acid evolved from Sample N under Different Conditions.*

Temperature in Dissolving.	Rate of Flow of Air per Hour.	Time of Boiling.	Result in Cubic Centimetres of $AgNO_3$ sol.
40°–50° C.	1 litre	1 hour	7·0
,,	1 ,,	next ½ hour	1·6
,,	6 ,,	1 hour	12·0
,,	6 ,,	next ½ hour	nil
100° C.	1 ,,	1 hour	13·1
,,	1 ,,	1 hour	14·6

Numerous experiments were next made to ascertain whether the hydrocyanic acid which remained in the solution after the sample had been dissolved could be estimated by precipitating the iron with a strong alkali, filtering, and titrating an aliquot portion of the filtrate. Efforts in this direction were not successful, however, as the precipitate of ferric hydrate always retained some of the cyanide. The addition of citric acid and ammonia to the nitric acid solution of the steel and the direct titration of the ammoniacal solution was also tried. This, too, was found to be of no value owing to the fact that the end point was difficult to detect with such small amounts of hydrocyanic acid.

Having thus failed to obtain an accurate method for estimating the whole of the hydrocyanic acid present in the nitric acid solution, it was decided to compare the amounts of carbon liberated in this form from various samples of normal and quenched steels in one hour's heating at 100° C. The conditions of each test were made as nearly alike as possible, 2·5 grammes of sample being dissolved at about 50° C., and a rapid flow of air maintained during the boiling. The results of these tests are given in the following table :

TABLE XI.—*Percentage of the Carbon present evolved as HCN in One Hour.*

Sample.	Carbon per Cent. in Sample.	Condition of Sample.	Percentage of the Total Carbon as HCN.
A	0·17	Normal	7·0
E	0·37	,,	4·5
J	0·54	,,	8·1
,,	0·54	Quenched	9·0
N	0·78	Normal	7·6
,,	0·78	Quenched	7·0
R	1·39	Normal	4·2
,,	1·39	Quenched [1]	4·9

Closely agreeing figures were obtained from duplicate tests made on several of these samples. As the results from the different steels were therefore too erratic to be accounted for by any slight difference in the conditions of the experiments, a second series of similar tests was made in order to find out whether the discrepancies were due to varying amounts of manganese in the carbide of the samples. The results of these tests, given in Table XII., proved conclusively that the quantity of hydrocyanic acid liberated was in no way connected with the percentage of manganese in the sample, and, consequently, that variation of the amount of manganese in the carbide was not the cause of the discrepancies. No explanation of the irregular ratios was found, but it will be observed that normal and quenched samples of the same steel yielded very similar amounts of the acid. It should also be stated here that the amount of nitrogen in these steels did not exceed 0·01 per cent. in any sample.

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[1] Austenitic sample.

TABLE XII.

Sample.	Carbon per Cent.	Manganese per Cent.	Condition of Sample.	Percentage of Total Carbon as HCN.
B	0·27	0·02	Normal	5·6
F	0·38	0·80	,,	6·6
K	0·55	0·02	,,	5·0
M	0·71	1·30	,,	6·2
,,	0·71	1·30	Quenched	6·6

A few experiments were also made in which the brown carbonaceous precipitate, formed on dissolving about 10 grammes of a steel high in carbon, was filtered, washed, and transferred to the apparatus A, B, (Fig. 2), with 50 cubic centimetres of dilute nitric acid. After heating this for thirty minutes at 100° C., the hydrocyanic acid which had been given off was estimated. In no instance was the amount obtained greater than that yielded by the first sample in Table XI. These experiments, therefore, clearly demonstrated that most of the hydrocyanic acid is formed in the early stages of the reaction.

Finally, a test was made to find out whether the carbon dioxide which is evolved can result from the action of nitric acid on the cyanide. 0·2 gramme of potassium cyanide was added to a solution of iron in nitric acid contained in the vessel A, B. The liquid was heated for a few minutes and a steady flow of air passed through it to drive off any carbon dioxide present as impurity in the cyanide. The apparatus was then connected with the absorption flask containing the barium chloride solution, and boiled for half an hour longer, during which time hydrocyanic acid continues to be given off. As only a trace of carbon dioxide was found to be evolved, it was concluded that the greater part of the carbon dioxide liberated in the Eggertz test was not derived from this source.

VII. THE AMOUNT OF CARBONACEOUS GAS OTHER THAN CO_2 OR HCN IN THE GASES EVOLVED.

It will be noticed, on comparing Tables II. and IV., that the average percentage of carbon given off as carbon dioxide is slightly lower than that obtained when the gases are passed over heated copper oxide. The experiments now to be described were made in order to determine whether this slight difference was due to the incomplete absorption of the hydrocyanic acid by the solutions of ferrous sulphate, or to the presence of small amounts of carbon monoxide or hydrocarbons in the gases.

The method employed in these experiments was precisely the same as that used in the preliminary tests (Section I.), with the exception that the ferrous sulphate solutions in D and E (Fig. 2) were replaced by strong solutions of caustic potash. By this means the whole of the carbon dioxide and hydrocyanic acid evolved were removed from the gases, and any precipitate of barium carbonate obtained in the absorption flask would be due, therefore, to the oxidation in the combustion tube of either carbon monoxide or hydrocarbon gas.

Blank tests were made by treating 1 gramme of pure iron and 0·05 gramme of calcium carbonate in A, B, (Fig. 2), exactly as described in the preliminary tests (Section I.), and passing the gases over the heated copper oxide. They consistently gave 0·004 gramme of barium carbonate. The samples and blank tests were heated at 100° C. for ten minutes in all cases, and after each test a fresh solution of caustic potash was placed in D.

TABLE XIII.—*The Amount of Carbon evolved as Carbon Monoxide or Hydrocarbon.*

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Weight taken.	Carbon per Cent. as CO or HC.	Percentage of Total Carbon as CO or HC.
			Grammes.		
N	Normal	0·78	1·5	0·025	3·20
,,	Quenched	,,	1·5	0·023	2·90
R	Normal	1·39	1·5	0·035	2·50
,,	Austenitic	,,	2·5	0·028	2·00
S	Normal	2·35	2·0	0·045	1·90

The results of these experiments are given in Table XIII., and it is evident that a small quantity of either carbon monoxide or a hydrocarbon (or both) was present in the gases given off in the first ten minutes' boiling. Three similar tests were next made in which the heating was prolonged from ten minutes to one hour. Three grammes of sample N quenched and also of sample R normal and quenched (austenite) were dissolved in 60 cubic centimetres of nitric acid, boiled for ten minutes, and the gases allowed to escape into the air. The apparatus was then connected with D and the boiling continued for fifty minutes longer. In each instance the weight of barium carbonate obtained did not exceed that given by a blank test. It is evident, therefore, that this carbonaceous gas is all evolved in the first ten minutes.

Experiments were also made on large amounts of the brown precipitate, which were prepared and treated exactly as described on page 22. As the weight of barium carbonate was not more than 0·005 gramme in any of these tests, it would appear highly probable that the gas under discussion arises from the initial action of the nitric acid on the iron carbide.

An attempt was next made to determine whether this minute quantity of gas consisted of a hydrocarbon or of carbon monoxide. The question unfortunately could not be settled by a volumetric analysis of the gases given off when the steel is dissolved, as large amounts of nitrogen are produced in the reaction and the carbonaceous gas can only be obtained in an extremely diluted condition. The method most suitable for the purpose seemed to be that in which iodine pentoxide at a temperature of 150° C. is used to oxidise small quantities of carbon monoxide when this gas is in a very diluted form. It was decided, therefore, to try this method of analysis, and details of the apparatus required were taken from a paper on the subject by E. H. Weiskopf.[1]

To obtain a sufficient amount of the gas for an investigation, about 30 grammes of a high carbon steel were dissolved in 600 cubic centimetres of dilute nitric acid, the temperature during the reaction being kept as low as possible. The liquid with suspended precipitate was then transferred to a 600 cubic centimetre flask provided with a ground-in glass stopper through which passed the exit tube. The flask and contents were next placed in a large vessel of boiling water, and as the temperature of the iron solution rose, a steady stream of gas was evolved. The gas which came off in the first ten minutes was collected in gas sample tubes filled with a strong solution of potassium permanganate to absorb the nitric oxide and peroxide. The heating was continued and further samples of the gas collected and treated in the same way.

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[1] *Chemical News*, 1909, vol. 100, p. 191.

Small portions of these samples were then withdrawn and analysed. They were found to consist almost entirely of carbon dioxide, nitrogen, and a little nitrous oxide, and very similar figures were obtained from both the quenched and unquenched steels used. Some typical results from sample R (combined carbon, 1·39 per cent.) are given in the following table:

TABLE XIV.

	Initial Gas.	Gas after Boiling 10 Min.	Gas after Boiling 30 Min.
	Per Cent.	Per Cent.	Per Cent.
CO_2 . . .	8·0	9·5	26·0
O . . .	nil	nil	nil
N_2O, N, and HC .	92·0	90·5	74·0

When the whole of the nitric oxides had been removed by the permanganate, the samples collected from the steel in the first ten minutes were transferred to another set of tubes containing strong solutions of caustic potash to absorb the carbonic acid. The volume of gas which was left after this absorption measured about 400 cubic centimetres at 18° C. in each experiment. The apparatus employed in examining these samples for carbon monoxide was as follows:

1. Mohr's bulb containing strong caustic potash solution.

2. Small glass trap filled with a clear solution of barium hydrate.

3. Mohr's bulb holding some strong sulphuric acid.

4. Small U-tube with ground-in glass stoppers. The tube was nearly filled with iodine pentoxide and was placed in glycerine which was kept at a temperature of 150° C.

5. Small glass trap containing a clear solution of barium hydrate.

6. Mohr's bulb containing strong caustic potash solution.
7. Combustion tube with heated plug of copper oxide.
8. Absorption flask, &c., containing the ammoniacal barium chloride solution.

The iodine vapour, which is given off when the pentoxide reacts with a carbonaceous gas, was not allowed to come in contact with any rubber tubing, as it strongly attacks rubber, causing the liberation of hydrocarbon gases.

The gas samples, collected and prepared as already described, were passed very slowly through this train of apparatus. In each experiment the first trap remained perfectly clear throughout, indicating that no trace of carbon dioxide was present. After the gases had passed through the pentoxide, a small precipitate of barium carbonate always appeared in the second trap. Any small quantity of carbon dioxide which might escape this solution was completely absorbed by the potash in the next bulb, so that the precipitate which came down in the absorption flask was undoubtedly due to the combustion, in the hot tube, of carbonaceous gas which had not been oxidised by the iodine pentoxide. After the apparatus had been well swept through with air, the precipitates of barium carbonate were collected and weighed. The results are given in the following table :

TABLE XV.—*Results obtained in Testing for CO with Iodine Pentoxide.*

Sample.	Carbon per Cent. in Sample.	Condition of Sample.	Amount of Gas Tested.	$BaCO_3$ in Trap after I_2O_5.	$BaCO_3$ in Absorption Flask.
			Cubic Centimetres.	Gramme.	Gramme.
R	1·39	Normal	410	0·012	0·017
N	0·78	Quenched	400	0·006	0·009

The accuracy of the method was tested by mixing 2 cubic centimetre portions of pure carbon monoxide with about 200 cubic centimetres of nitrogen and passing the mixtures through the apparatus. In these tests, however, the absorption flask was connected directly with the pentoxide tube and the combustion tube was left out. The iodine vapour on leaving the U-tube was condensed in a small glass trap which was kept quite cold.

In each experiment the carbonic oxide used was found to have been completely oxidised by the iodine pentoxide at 150° C. If, therefore, the carbonaceous gas in the gases collected from the steel samples had existed as carbon monoxide it also should have been entirely oxidised by the pentoxide, which was by no means the case. Moreover, since it appears[1] that hydrocarbons themselves can be partially oxidised by this reagent, it is doubtful whether any of the precipitate obtained in the barium hydrate trap (Table XV.) resulted from the oxidation of carbon monoxide. As hydrocarbon gas was certainly present in these samples, it is hardly to be expected that it would completely escape the action of the pentoxide.

The evidence appears to be fairly conclusive, therefore, that the gases given off in the Eggertz test contain, in addition to carbon dioxide and hydrocyanic acid, a very small quantity of a hydrocarbon, and only a trace, if that, of carbon monoxide. This hydrocarbon is insoluble in ferrous sulphate and caustic potash solutions and arises from the solution of the carbide, but it is not liberated unless the nitric acid solution of the steel is heated.

VIII. Estimation of the Total Carbon in the Evolved Gases.

The results of the work already described clearly indicate that the gases given off from both normal and quenched steels (also intermediate conditions), when these are dissolved in dilute nitric acid and the solutions heated, contain carbon dioxide, hydrocyanic acid, and a trace of hydrocarbon gas; and, moreover, that the ratio of the carbon dioxide and of the hydrocarbon gas to the carbon in the steel is practically constant in all cases, with the exception of the austenitic steels. While these results are in agreement with the work of Osmond and Werth[2] so far as the nature of the carbon compounds is concerned, they differ seriously as regards the quantities of the compounds found to be liberated, especially in the case of the hydrocarbon gas. The authors referred to state that this gas is given off in much greater amount from quenched steels, and, as a consequence, the idea was formed that the "missing" carbon of the quenched steels is contained in the gases evolved on dissolving.

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[1] *Chemical News*, 1909, vol. 100, p. 274.

[2] *Loc. cit.*

It was decided, therefore, to make a final series of tests in which the whole of the gases liberated should be passed over the heated copper oxide without any intervening absorbent, so as to obtain their total carbon content, including any easily condensable carbonaceous gas, if such were present.

For this purpose a piece of thick-walled silica tube was used, about 15 inches long, and of the same pattern as that shown in E, Fig. 1. The narrow end was about 3 inches long, and was connected by means of a short piece of glass tubing with the exit tube of the special apparatus A, B, Fig. 2. A plug of oxidised copper gauze 2 inches long was fitted into the silica tube at the end of the wider part adjoining the narrower. A piece of wide glass tubing over which was placed a short length of rubber tubing was tightly fitted into the wider end of the silica tube, which was about 1 inch in internal diameter. The glass tube was about 4 inches long, and contained two small bulbs which acted as traps to collect the condensed acid vapours which passed over. The remainder of the apparatus consisted of the vessel F, Fig. 2, containing a strong solution of potassium permanganate, and the absorption flask, &c. The above type of combustion tube was employed in order to avoid the use of rubber corks, and to expose a minimum amount of rubber to the action of the gases. The procedure in all the experiments was as follows:

One gramme of sample was placed in the bulb B of the vessel A, B, Fig. 2, which was then connected with the air-purifying train and the combustion tube. The gas was lighted under the copper oxide and a clear solution of ammoniacal barium chloride next prepared as previously described. 20 cubic centimetres of nitric acid (1·12 sp. gr.) were then slowly forced into B; a vigorous reaction was avoided by dissolving the sample very slowly, and in order to ensure the presence of some oxygen in all the gas as it entered the combustion tube, a steady flow of air was maintained throughout. After the sample had dissolved, the water in the basin was brought to the boil and boiled for exactly ten minutes. The tripod and basin were then quickly replaced by another tripod and basin containing cold water. Finally the narrow end of the combustion tube and glass tube connected with it were heated with a spirit flame until the whole of the liquid condensed in them had been driven over the hot copper oxide. After the apparatus had been well swept through with air the barium carbonate precipitate was collected and weighed.

Blank tests made on a pure iron sample repeatedly gave 0·006 gramme of barium carbonate. In one instance the gases from a blank test were passed over 0·05 gramme of pure calcium carbonate which was being heated in the combustion tube. The correct amount of barium carbonate was obtained, showing that the carbon dioxide present in the gases was being completely precipitated in the ammoniacal solution.

On reference to Table XVI. it will be seen that the total amount of carbon, found by the above method, in the gases from normal and quenched samples of the same steel is practically the same. None of the quenched steels gave more than 60 per cent. of the colour given by the normal steel in the Eggertz test. If, therefore, the "missing" carbon had been contained in the gases evolved, a very much greater weight of precipitate should have been obtained from these quenched samples.

It will also be observed that the ratio of the carbon in the gases to the amount present in the steel approximates closely to the sum of the ratios already found for the carbon dioxide, hydrocarbon gas, and the variable hydrocyanic acid. Evidently these compounds are the only forms in which the carbon is liberated when a steel is dissolved in dilute nitric acid.

TABLE XVI.—*Total Amount of Carbon in the Gases evolved in Ten Minutes' Heating.*

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. (all forms) Liberated in 10 Min.	Percentage of Total Carbon Evolved.
J	Normal	0·54	0·146	27·0
,,	Quenched	0·54	0·152	28·0
M	,,	0·71	0·195	27·5
N	Normal	0·78	0·235	30·0
,,	Quenched	0·78	0·235	30·0
R	Normal	1·39	0·383	27·5
,,	Quenched	1·39	0·380	27·4

IX. The Oxidation of the Carbon remaining in the Solution by Means of Potassium Permanganate.

It is obvious that as the quantities of carbon in the gases from quenched and normal steels are the same, the amount which remains in the solution in each case must also be the same, notwithstanding the great difference in the colour-values. In order to obtain direct evidence that the "missing" carbon is actually present in the solution, experiments were made to ascertain whether the whole of the carbon contained in it could be expelled as carbon dioxide by the addition of a strong oxidising reagent. After a number of trials with several substances it was found that the addition of a saturated solution of potassium permanganate yielded the best results. Not more than about 80 per cent. of the carbon left in the solution could be obtained by this means, however, and the addition of strong nitric acid along with the permanganate gave no further increase; the procedure was as follows:

Table XVII.—*The Carbon obtained from the Solution by Oxidation with* $KMnO_4$.

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Carbon per Cent. by Colour.	Carbon per Cent. in Gases.	Carbon per Cent. Oxidised	Total per Cent. Obtained.	Percentage of Total Carbon Obtained.
J	Normal	0·54	0·54	0·146	0·335	0·481	89·0
,,	Quenched	0·54	0·32	0·152	0·323	0·475	88·0
N	Normal	0·78	0·78	0·235	0·444	0·679	87·0
,,	Quenched	0·78	0·42	0·235	0·404	0·639	82·0
R	Normal	1·39	1·40	0·383	0·865	1·248	89·0
,,	Quenched	1·39	1·00	0·380	0·798	1·178	85·0

A saturated solution of the purest potassium permanganate obtainable was made and filtered through an ignited asbestos pulp. It was kept in a stoppered bottle.

One gramme of the sample was dissolved in 20 cubic centimetres of dilute nitric acid, in the special apparatus A, B, Fig. 2, and boiled for ten minutes, during which period a steady stream of purified air was passed through the solution. The apparatus was then connected with the absorption flask containing the ammoniacal barium chloride solution which had been previously prepared. The heating was continued for twenty minutes longer, and during that time 6 cubic centimetres of the permanganate solution was gradually added to the liquid. After the apparatus had been well swept through with air, the precipitate of barium carbonate was collected and weighed.

Blank tests were made by adding the same quantity of permanganate to solutions of pure iron. Table XVII. gives the results obtained in these experiments. It was found that the carbon which was expelled was all in the form of carbon dioxide.

It will be seen that although slightly lower amounts were obtained from the quenched samples, the results, nevertheless, furnish conclusive evidence that the "missing" carbon is contained in the nitric acid solution and does not escape as a gas.

PART III.

THE EGGERTZ TEST.

In making the Eggertz test the details can be varied somewhat, although the reactions involved are in all cases the same. It will be as well, therefore, at the outset, to describe the particular method used in this investigation.

0·5 gramme of the sample is treated in a 6-inch by 1-inch test tube with 10 cubic centimetres of dilute nitric acid (1·2 sp. gr.). The tube is placed at once in cold water and allowed to remain there until the steel has dissolved. It is then put into boiling water and boiled[1] for fifteen minutes. After cooling, the colour is compared with that of a standard steel solution which has been prepared along with the sample and treated in exactly the same way. The colour test is made in 100 cubic centimetre comparison tubes of equal bore (about 1 inch diameter). The standard is diluted with water to a volume in cubic centimetre equal to two hundred times its percentage of carbon and placed in one of the tubes. The sample is placed in the other tube and diluted to the same depth of colour ; its volume is then measured and on dividing by two hundred the required percentage of carbon is obtained. The colour comparison is made by holding the tubes together before a piece of white filter paper of fine texture and examining the tints against a good light. It is convenient to train the eye, so that, when the colours are exactly matched, the left-hand tube (or the right-hand tube) will always appear to be a slight shade darker than the other, no matter which tube may occupy that position.

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[1] The word "boiled" when used in this connection, in the present report, is always employed to indicate that the sample tube was heated in boiling water, *i.e.* at 100° C.

I. A Standard Tint Series.

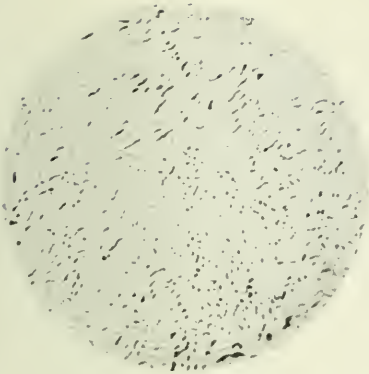
As is well known, some samples, especially quenched steels, give rise to a greener tint than others. In order to provide some record of the tints observed in these experiments, a set of permanent standards was made up in a series of 1-inch comparison tubes of equal internal diameter. The following solutions were used :

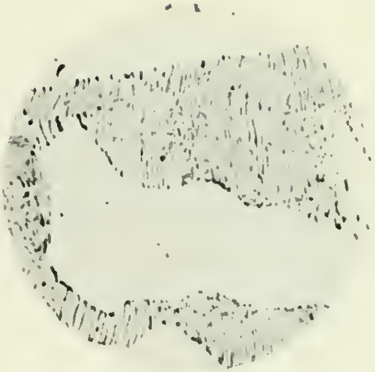
A. 25 grammes of pure iron dissolved in 500 cubic centimetres of nitric acid (1·2).

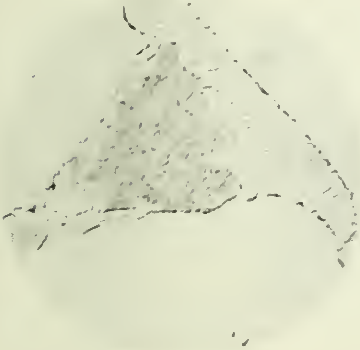
B. 2 grammes of metallic cobalt dissolved in 20 cubic centimetres of nitric acid and made up to 500 cubic centimetres with water.

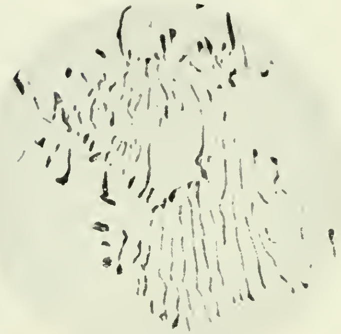
Each standard was made by taking 20 cubic centimetres of solution A, 20 cubic centimetres of sulphuric acid (1–3 aq. by vol.), mixing and diluting to 50 cubic centimetres with water. Gradation of tint was obtained by adding to these standards 5, 6, 7, 9, 11, and 13 cubic centimetres of solution B. The tint numbers which will be given below refer to the number of cubic centimetres of solution B required to make the standard match the colour under investigation. Such a tint-series is, of course, quite arbitrary in character. The matching of the greener with the browner colours has always been a source of difficulty, and leads to ambiguity in the value for the " missing " carbon, as found by matching a greenish solution against a browner standard. It is not easy to give a precise interpretation to the well-known recommendation of Eggertz to dilute " to the same depth of tint " colours which are not quite the same. Different observers do, in fact, obtain somewhat varying results when asked to match two dissimilar colours in this way. The above tinted solutions,

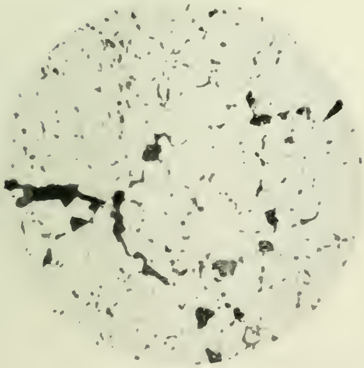
PLATE I.

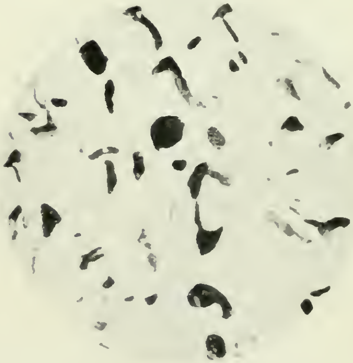

No. 1. (*See page* 35.)


No. 2. (*See page* 71.)

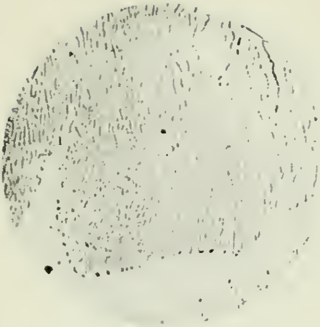

No. 3. (*See page* 72.)


No. 4. (*See page* 72.)

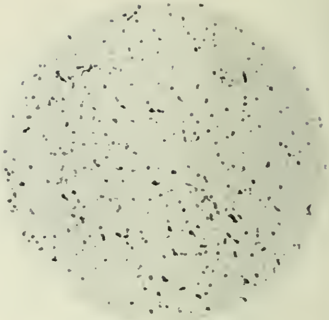

No. 5. (*See page* 62.)


No. 6. (*See page* 36.)

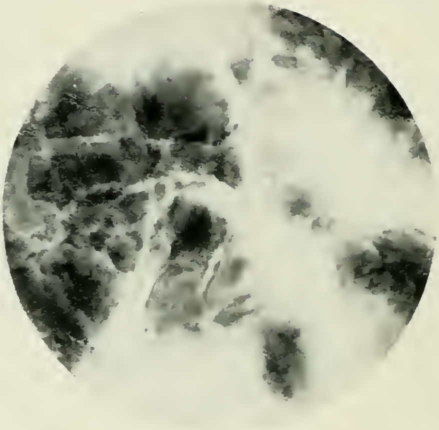
Magnified 1,250 diameters and enlarged by one-third.



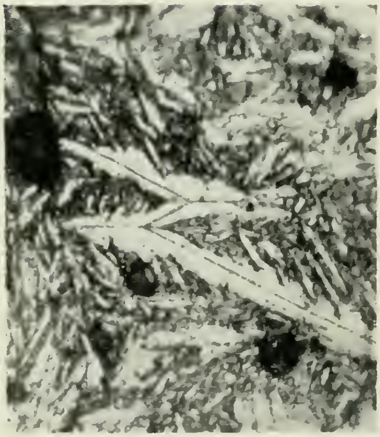
No. 18. (*See page 97.*)



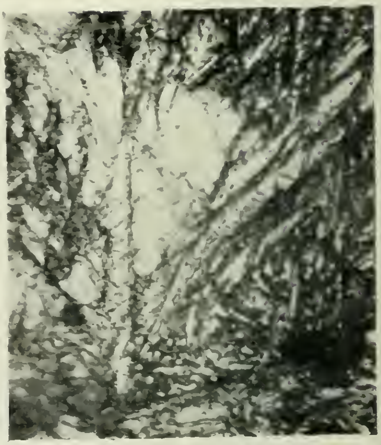
No. 19. (*See page 95.*)



No. 20. (*See page 87.*)



No. 21. (*See page 18.*)



No. 22. (*See page 18.*)

Nos. 18, 19, 21, 22 magnified 1,250 diameters.
No. 20 magnified 500 diameters.
Enlarged by one-eighth.

on comparison with one another, appeared to be of equal intensity in colour to three observers, and were therefore employed as a standard series for the matching of different tints.

The tints obtained from various samples in the Eggertz test range between Nos. 7 and 11 in the series, and, when the comparison is made in 100 cubic centimetre comparison tubes, the resemblance of these colours to the colours given by the steels is very close. All comparison must be made in diffused daylight; the spectrum of the standards is not identical with that given by the Eggertz tints, so that artificial light cannot be used. These iron solutions have an appreciable temperature coefficient, the colour increasing with the temperature at the rate of 1 per cent. per degree at 18° C. The comparisons recorded in this Report were all made at about that temperature.

II. The Action of Nitric Acid on the Carbon in Steel Drillings.

On adding the nitric acid to a normal sample and keeping the liquid quite cold by constantly shaking the test tube in a stream of cold water, a black precipitate forms as the steel gradually dissolves. This precipitate is produced by such treatment from all samples in which the carbide particles, when stained with sodium picrate, can be detected under the microscope. It is not sufficient merely to place the tube in a vessel containing cold water, as the temperature of the acid can rise considerably under such conditions owing to the heat generated by the chemical action; the black precipitate in some cases may not then be obtained. Constant and vigorous agitation must be given in order to keep the solution quite cold throughout.

On standing, even at room temperature, the colour of the precipitate slowly changes from black to brown. The speed of the change is, of course, greatly accelerated by heating. It is well known that the alteration is due to the removal of iron from the black precipitate. The formation of this precipitate and its conversion to the brown state was first accurately described by Parker.[1]

Four estimations were made of the carbon and iron in the brown precipitate prepared at 18° C. from different steels. The precipitate was collected on an asbestos felt in a small Gooch crucible, washed, and dried in a desiccator. The carbon content was found by combustion and the iron estimated in the residue. The results of the four determinations were in close agreement, the average being: carbon, 51·5 per cent.; iron, 2·5 per cent. The analysis of this precipitate as given by T. W. Hogg[1] showed: carbon, 49·41 per cent.; iron, 2·54 per cent. And by Juptner:[2] carbon, 44·59 per cent.; iron, 8·05 per cent.

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[1] *Chemical News*, 1880, vol. 42, p. 88.

It was observed that the weight of the brown precipitate decreased by about 10 per cent. when heated at 60° C. after completely drying in a desiccator at room temperature, but afterwards between 60° C. and 90° C. the loss in weight was very slight. Some experiments were therefore made in order to find out whether any loss of carbon occurred at these temperatures. A quantity of the precipitate was prepared, in each case, from 10 grammes of sample N, filtered on to an ignited asbestos pulp, and most thoroughly washed with water. The precipitate was then placed in the wide limb of a U-tube specially devised to allow the substance to be heated in a slow current of pure air. The flask containing the ammoniacal solution of barium chloride, prepared as described in Part I., was connected directly with this tube to collect any carbon dioxide which might be given off by the precipitate. It was found that, in drying, even at 70° C., a slight but appreciable amount of carbon dioxide was liberated. This loss of carbon is probably due to the retention of some nitric acid by the gelatinous substance of which the particles of the precipitate are composed. In determining the nitrogen content of this brown substance, the possibility of the adsorption by the precipitate of both nitric acid and ferric nitrate seems to have been overlooked by previous investigators.

On testing the initial black precipitate for its carbon content, a large but variable quantity of ferric oxide was always left after the ignition. The amount of carbon found was equal to about 50 per cent. of the loss in weight, just as in the case of the brown precipitate. For example, 0·056 gramme dried at 70° C. weighed after ignition 0·044 gramme and yielded 0·006 gramme of carbon.

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[1] *Journal of the Iron and Steel Institute*, 1896, No. II. p. 179.

[2] *Ibid.*, 1897, No. I. p. 248.

When dried in the desiccator the black precipitate was found to be magnetic, a fact first noted by Hogg. It therefore contains either magnetic oxide of iron, or undecomposed carbide, or possibly both.

The time of change, at 18° C., from the black to the brown condition was found to depend greatly upon the degree of fineness of the particles of carbide in the steel, and varied from a few minutes to twenty-four hours. An examination of the precipitate under the microscope revealed the fact that its component particles resembled, to a marked degree, the particles of cementite from which they were formed. In making the comparison, polished specimens of various steels were lightly etched with picric acid and then treated for ten minutes with a boiling alkaline solution of sodium picrate to stain the carbide. The precipitate from each steel, in an intermediate condition between the black and brown state, was filtered, washed, and mounted in water on glass slips for microscopic examination.

The fine lamellar and bacillary pearlite, shown in photo. 1, was found to give large clusters of extremely thin flat sheets and rod-shaped pieces of the brown compound. Typical examples, prepared from sample N, are given in photos. 7 and 8. The former has undoubtedly been produced from lamellar pearlite and the latter most probably from the bacillary form ; under the highest magnification the surfaces of the lamellæ are seen to be evenly striated. It is quite evident, in both instances, that the individual pieces of precipitate are much larger than the carbide particles from which they were formed. This swelling of the substance always accompanies the change of extremely small particles of carbide to the brown compound and appears to be due to excessive hydration. When the substance is in this condition the component pieces very strongly tend to adhere to each other and so form large aggregations. At 18° C. the greater part of the associated iron is quickly removed by the nitric acid from this type of precipitate, and the gases escaping from the liquid become entangled in the aggregations, and cause them to rise to the surface.

On the other hand, coarse particles of cementite give rounded masses of the precipitate which appear much deeper in colour owing to the retention of more iron. Examples are shown in photos. 10 and 11, the former being prepared from the coarse carbide seen in photo. 5 and the latter from that shown in photo. 6. The precipitate shown in photo. 9 was obtained from sample N (photos. 1, 7, 8) after it had been annealed for twelve hours at 680° C., to divorce the pearlite. It will be noticed in these instances that the formation of the brown substance has not been accompanied by any great amount of swelling. The iron contained in these denser particles is held much more tenaciously than in the more hydrated forms from the finer carbide, and its removal in the cold by the acid requires about twenty-four hours. Particles of this size and condition do not adhere to each other to any marked degree, and in the black state, being heavily weighted with iron, they sink to the bottom of the solution on standing.

The great difference in the amount of hydration, and consequent degree of swelling, of the precipitates from the fine and coarse particles of cementite is difficult to explain, but it was repeatedly observed that as the size of the carbide increased the swelling of the precipitate rapidly diminished.

Seeing that the change in colour of the precipitate from black to brown is due to the removal of iron by the acid, and takes place more and more quickly as the size of the carbide decreases, it is to be expected that, when the carbide reaches a certain degree of fineness, the black precipitate will no longer be observed on dissolving the drillings, owing to the change to brown taking place too rapidly. If a sample of steel (combined carbon, about 0·30 per cent.) is quenched from 800° C., and reheated at 400° C. for about twenty minutes, this condition can be produced ; as the period of reheating is increased the black precipitate again begins to appear in the test on dissolving.

To remove the excess of iron from the precipitate, the nitric acid must of necessity diffuse throughout the particles. That this process of imbibition takes place is also shown by the fact that the carbon dioxide obtained by heating sample E (photos. 6 and 11) for five minutes at 70° C. was in approximately the same ratio as in the other steels, although in this case most of the brown precipitate remained undissolved (see Table III., Part II.). The effect of nitric acid and iron on the precipitate will, however, be more fully discussed later.

The particles of the black precipitate contain practically the whole of the carbon present in the carbide particles from which they were formed. This was proved by dissolving 1 gramme portions of sample E (combined carbon, 0·37 per cent., photos. 6 and 11) in 20 cubic centimetres of nitric acid (1·2 sp. gr.) in the cold and filtering the black residues on an ignited asbestos pulp. In each case the filtrates on dilution were colourless and the carbon obtained by the combustion of the residue, after drying at 70° C., amounted to 0·36 per cent. out of a total of 0·37 per cent. contained in the steel. It should be mentioned, in passing, that this experiment shows that α-iron can hold very little carbide in solution.

III. The Solution of the Precipitate.

On allowing the nitric acid solution of the steel to stand, the brown precipitate begins gradually to disappear, and a brown solution is formed. At 15° C. several months may elapse before a clear liquid is obtained, but with increasing temperature the reaction quickens, and at 100° C. it can be completed in the majority of cases within fifteen minutes. On comparison of the periods required by various steels before a perfectly clear solution was obtained at 100° C., it was found that those samples containing very large particles of carbide always took the longest time. For example, the precipitate from the pearlite in photo. 1 dissolved in about one-half the time necessary for that shown in photo. 6. Intermediate cases, however, do not always behave in a like manner, and marked differences in the size of the carbide may not give rise to any difference in the rates of solution, for the reason that the agglomeration of the particles of the precipitate which takes place also has a retarding effect, most probably because it reduces the area of the surfaces exposed to the acid. This question will be referred to again in Part IV. In making the colour test on steels containing the coarsest particles, as shown in photo. 6, the solution at 100° C. acquires a peculiar muddy appearance, which is easily detected, and is caused by suspension in the liquid of the unagglomerated rounded particles of the precipitate.

If the carbon in quenched steels still exists as carbide (Fe_3C)

in solid solution it must admittedly be in a molecular state of division. Hence, the particles of brown compound formed from it by the action of the nitric acid must also be in an exceedingly fine state, and should pass at once into solution on dissolving. It is certainly the case that quenched steels give very little brown precipitate, the greater part of the carbon passing directly into the acid solution, which becomes brown in colour. The fact that a slight brown precipitate can always be obtained, even from the most rapidly quenched samples, can be explained as due either to agglomeration, or else to the presence in the metal of some undissolved or reprecipitated carbide. This slight precipitate dissolves very rapidly on heating.

Results obtained by the employment of much weaker acid to dissolve the steel furnish interesting evidence in this connection. Samples of normal steels, when slowly dissolved at 15° C. in solutions containing 10 per cent. of strong nitric acid, yield brown precipitates, the particles of which are identical in shape with those obtained from the same steels with stronger acid. Quenched steels also yield a brown precipitate which, on examination under the microscope, is found to consist entirely of lumps of a transparent colloidal substance as shown in photo. 20. These brown masses split up easily under pressure and appear quite structureless under the highest magnification.

It is clear, therefore, that the molecules of the carbide (or carbon) in quenched steels are first transformed into a brown substance which is not readily dissolved in weak acid, and the minute particles have then time to agglomerate into gelatinous masses. The precipitates obtained, both from quenched and normal steels, by the use of weak acid dissolve very slowly in nitric acid (1·2 sp. gr.), at 100° C., with the liberation of small quantities of carbon dioxide.

A method for estimating "hardening" carbon in steels, based on the fact that the "hardening" carbon in quenched steels dissolves in dilute nitric acid (1·2), with the formation of very little precipitate, was suggested by Jüptner.[1] The sample is dissolved in the cold, the solution filtered, and the amount of colour in the filtrate estimated against a standard. Later, Campbell and Haskins[2] state that results obtained in this manner

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[1] *Loc. cit.*

[2] *Journal of the Iron and Steel Institute*, 1913, No. II. p. 367.

"are due to the total colour of the dinitro-derivatives from carbides soluble in the cold."

It is by no means certain, however, that the smaller particles of free cementite present in the steels are not also represented as "hardening" carbon by this method. On treating fine and coarse drillings of sample M in the manner recommended by the above authors, it was repeatedly found that the fine drillings gave a higher colour value. Thus the extra colour obtained must have been an effect due to the solution of some free carbide, for the quantity of "hardening" carbon (*i.e.* carbon in solid solution) could not have differed in the two cases. As, therefore, free carbide can give rise to additional colour under this slight change in conditions, it cannot be taken for granted, when coarse drillings are used, that the cementite is entirely insoluble in the acid, and that the colour of the filtrate is due to "hardening" carbon alone. (See also Part IV., p. 97.)

IV. The Coloured Products in the Solution.

There are several facts which definitely indicate that the colour of the solution when diluted is caused by organic substances in colloidal suspension; mention may be made of the following:

1. The tendency of the diluted solutions to froth.
2. On filtering undiluted solutions a brown stain is always left on the filter-paper.
3. On filtering the liquids through animal charcoal, almost the whole of the colouring matter is removed by adsorption.
4. On shaking the undiluted solution with iso-amyl alcohol, the colouring matter is transferred to the latter and is then often precipitated at the interface.

The above effects, which can be observed with solutions of both quenched and normal steels, suggested that the examination of the coloured solution by the method of dialysis might be useful in the investigation of some of the problems connected with the test.

Dialysis of the Solution.—The first attempts in this direction were made by dissolving 1 gramme portions of a normal and a quenched sample of the same steel in nitric acid (1·2), boiling, and placing the clear solutions in two small parchment dialysers which were suspended in about 30 cubic centimetres of distilled water. It was found that, in both cases, the water acquired a greenish tint, but although some of the iron passed through the membrane, most of it remained inside with the colouring matter.

Attention was next directed, therefore, to the dialysis of the nitric acid solution of the brown precipitate apart from the iron. It has already been shown that the whole of the colour given by annealed steels is derived from the solution of this substance (p. 37). To prepare a sufficient quantity for the purpose, 15 grammes of a steel, containing about 1·2 per cent. of carbon, were dissolved in 300 cubic centimetres of nitric acid (1·2), the solution being kept as cool as possible during the reaction. The bulky brown precipitate was filtered off, well washed with water, and then washed off the paper into a beaker. The water containing the precipitate was next evaporated to about 18 cubic centimetres by boiling and transferred to a large test tube ; 12 cubic centimetres of strong nitric acid were added, and the tube placed in boiling water for twenty minutes or so. The dark red liquid obtained was finally filtered and dialysed. In dialysing, the collodion bags recommended by Taylor[1] were found to be very suitable and greatly preferable to parchment, as the effects could be watched through the transparent membrane. The bags were made to hold about 30 cubic centimetres and were attached to suitable glass tubes so as to allow them to be suspended in distilled water.

When the prepared solution of the precipitate is placed in the bags, the acid begins to diffuse rapidly into the surrounding water. This steady removal of the acid from the liquid in the bag causes a reddish-brown precipitate gradually to appear and, as the action proceeds, the outside water acquires a greenish colour. By changing the water three or four times at intervals of about twelve hours, the whole of the acid can be removed, but, even after the fourth change, the whole of the colour is not removed from the liquid within and the water outside still becomes green.

The nitric acid solution of the precipitate can thus be divided by dialysis into three parts, viz. :

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[1] "Chemistry of Colloids," p. 28.

A. A reddish-brown or chocolate-coloured precipitate.

B. A yellow-green solution which diffuses through the dialyser.

C. A brown-coloured solution within the dialyser.

The collodion bag is itself strongly stained by the colouring matter, which is only partially removed by prolonged soaking in water. For this reason a quantitative separation of the substances cannot be obtained by dialysis. The precipitate A is readily filtered off and easily redissolves in warm nitric acid (1·2). If the solution so obtained is immediately dialysed in a new bag, the precipitate is quickly thrown down again, but in lesser quantity, on the removal of the acid, and the solution within the bag remains coloured as before. No green-colour appears in the surrounding water. If, however, the nitric acid solution of the precipitate A is heated at 100° C. for about two hours and then dialysed, no precipitation occurs within the bag but almost all the colouring matter passes into the surrounding water as green solution B. It is evident, therefore, that on boiling the brown precipitate A in dilute nitric acid it is slowly and completely changed into the soluble green substance B.

The Colours of the Products of Dialysis in Terms of the Tint Series (p. 32).—The nitric acid solution of the precipitate A has about tint 8; the green diffusion B is difficult to match but is greener than tint 4. The solution C has usually tint 6–7 after the precipitate has been separated from it; but, if it be redialysed in a new bag so as to remove the residual green substance B, it attains exactly the same tint in nitric acid (1·2) as the solution of the precipitate.

Reactions with Ammonia.—On addition of ammonia in excess to the solution of the dialysed precipitate any iron present is thrown down, on boiling, as ferric hydrate, which always occludes a little of the colouring matter. A comparison can be made of the colour-intensity of the acid and alkaline solutions, by filtering off this precipitate, dividing the filtrate into two equal portions, and re-acidifying one with nitric acid. Repeated tests showed that the colour-ratio of the alkaline and acid solutions of the precipitate is as 1·25 : 1·0. The green diffusion B can be concentrated by boiling and, when tested similarly, the colour-ratio of the alkaline and acid solutions was found to be just double the above, *i.e.* 2·5 : 1·0. The filtrate C gave an intermediate value, but after dialysing a second time the ratio obtained was the same as that from the precipitate A. This solution may thus be regarded as a colloidal (emulsoid) form of the brown precipitate A containing, on first dialysis, a small quantity of the green substance B. There is therefore no further need to consider it separately.

The Existence of Two Colouring Compounds.—The very marked and constant difference in the behaviour of the reddish-brown precipitate and yellow-green diffusion strongly indicates that the substances are two distinct chemical compounds;[1] the reaction with ammonia and conversion from the brown to the green by the action of nitric acid suggests that they are nitro-derivatives of a complex hydrocarbon group. No attempt has been here made to ascertain their constitutional formulæ; in the present Report the brown compound will be referred to as substance A and the green compound which diffuses through the dialyser as substance B. It should be noted that the latter substance, when in concentrated solution, has an orange colour and only becomes yellow-green on dilution.

The Increase of Colour due to the Presence of Iron.—In the ordinary Eggertz test the concentration of the iron in the solution is always the same. To investigate the effect of a varying concentration of iron, two portions of the same sample were taken and additional pure iron was added to one. In dissolving, the amount of nitric acid used in the test was increased on account of the extra iron added, so that, while the amount of free acid remained about the same in both cases, the quantity of iron varied. After the samples had been boiled more nitric acid was added in equal amounts to each to prevent any coloration of the solution by the extra amount of iron added.[2] The results given in Table XVIII. were obtained by matching the two tests prepared in this way. In all cases the colour was increased by the addition of iron and it was also found that the tints became browner.

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[1] It is, of course, possible that each may be a mixture of several colouring compounds, but the constancy of their properties in the various preparations which were made is rather against this view.

[2] In the Eggertz test (p. 31), with carbons higher than 0·12 per cent., the dilution is sufficient to remove all iron coloration.

TABLE XVIII.—*Effect of increased Iron in the Test.*

Sample.	Condition of Sample.	Amount Taken.	Extra Iron added.	HNO_3 (1·2) used to Dissolve.	Additional HNO_3 (1·2) after Boiling.	Colour-Value.
		Gramme.	Gramme.	Cubic Centimetres.	Cubic Centimetres.	Cubic Centimetres.
E	Normal	0·25	...	5·0	3·0	40
,,	,,	0·25	0·15	6·0	3·0	45
N	Normal	0·25	...	5·0	3·0	78
,,	,,	0·25	0·135	6·0	3·0	92
M	Quenched	0·25	...	5·0	3·0	40
,,	,,	0·25	0·15	6·0	3·0	44
P	Quenched	0·25	...	5·0	3·0	45
,,	,,	0·25	0·14	6·0	3·0	50

Another series of tests was made on a nitric acid solution of the brown precipitate which had been separated from the iron by filtration. The addition of iron to this solution also increased the colour and the tint became browner.

It thus appears that the colour of the Eggertz test is dependent not simply upon the formation of coloured carbon compounds, but also upon the interaction of these compounds with the iron in the solution. In view of the indications that the colouring substances are nitro-compounds some experiments were also made on the effect of nitrous acid on the colour. Tests were prepared in which large quantities of potassium nitrite were added both during and after the solution of the steel. The copious fumes of nitrous acid evolved had no influence either upon the tint or the colour-value.

ADSORPTION ?

For the closer study of the influence of the iron on the tint and colour-value, experiments were made in order to ascertain the effect of iron upon the substances A and B, into which the colouring matter of the Eggertz test can be divided by dialysis. The addition of iron to these substances can be made in two ways, either by dissolving the metal in the solution of the compound made to 1·2 sp. gr. with nitric acid, or by dissolving the metal first in nitric acid and then mixing the two solutions. For the latter method, a standard solution was prepared, containing 0·5 gramme of pure iron and 4·0 cubic centimetres concentrated nitric acid in each 7·0 cubic centimetres. Dilute solutions of iron in nitric acid in these proportions are practically colourless, but, with increasing concentration either of nitric acid or of iron, the colour due to the iron may cause serious error. In the following experiments blank tests were made where required to ensure the absence of such errors.

Effect of Iron on Solutions of Substance A.—To equal portions of a solution of substance A (brown precipitate) in nitric acid (1·2) were added varying amounts of metallic iron. When the metal had dissolved the tests were diluted and compared, one being taken as standard. The effect of these additions of iron is shown in curve A, Fig. 4. The colour was deepened a little and became slightly browner, changing from about tint 8 to 9 as the iron was increased. The addition of the iron as standard solution to a second series of tests produced a very similar result.

Effect of Iron on Solutions of Substance B.—Varying amounts of iron as metal were next added to equal portions of a solution of substance B (green diffusion). This solution was first concentrated to about the same colour-intensity as that of A above and brought to 1·2 sp. gr. with nitric acid. The result is given in curve B_2, Fig. 4. It will be seen that here a very large increase of colour occurs, accompanied by a marked change of tint as indicated by the tint-numbers on the curve. It was, however, repeatedly confirmed by direct comparison, that, with the Eggertz concentration of iron and nitric acid, the tint of substance B is always greener than that of substance A. The addition of iron as standard solution to substance B also causes a large increase of colour, but not so great as when metallic iron is added, as shown in curve B_1, Fig. 4, and the tint produced is not quite so red. In making these tests, the solution of B contained only 1 cubic centimetre of nitric acid (1·2) in 5 cubic centimetres. With increasing concentration of nitric acid the colour-intensity produced by the addition of iron solution is slightly lowered.

The very noticeable difference between the curves B_1 and B_2 is due entirely to the form in which the iron was added to the solution. The surplus colour which results from adding the iron as metal is very remarkable, and the subject will be further discussed in connection with the effect of additions of nitric acid to these solutions (p. 47).

The curves B_1, B_2 have a very distinctive form and strongly resemble an "adsorption curve," an important characteristic of which is that the greatest increase occurs at the beginning. It is, however, admittedly difficult to distinguish between adsorption and the weaker types of chemical combination, and whether the reactions of the green substance B with iron are to be ascribed to one or other of these causes, or to variations in the nitro-compounds themselves, has not been finally decided by the experiments here described. Somewhat similar results are observed on adding iron to nitric acid solutions of salicylic and gallic acids. Further information might be obtained by the comparison of such reactions with those of the colouring matters A and B described above.

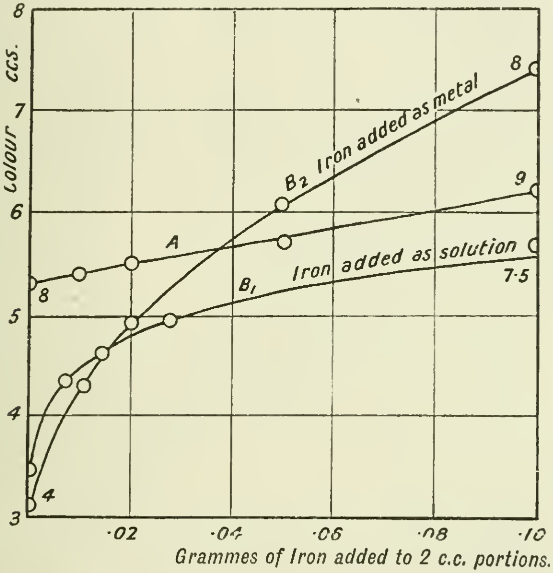

FIG. 4.—Influence of Iron on Coloured Compounds.

EXPERIMENTS ON REVERSIBILITY.

Throughout the preceding experiments it has been tacitly assumed that the colouring power of the substances in the Eggertz test solution is unaffected by dilution; but, since it has been shown that the colour is partly due to a reaction between the colouring matter and the iron in the solution, the irreversibility of the reaction cannot be taken for granted. Three variable concentrations are involved, those of iron, nitric acid, and the colouring matter, and it will only be possible to examine a few selected cases.

Dilution with Water.—It is generally recommended in descriptions of the Eggertz method that the test should not only be made against a standard steel having the same heat treatment as the sample, but also against one having a similar carbon content. When two steels differ in carbon the dilution of the tests will, of course, vary proportionately and, if the reaction is not irreversible, a certain amount of error might be introduced.

A series of tests was therefore made in which differing amounts of the same steel (0·10 to 0·50 gramme) were weighed and sufficient pure iron to make 0·5 gramme added to each. The colour-carbons were then found by the method on p. 31. A second series was also made by taking varying quantities of a clear solution of steel S in nitric acid (1·2) and adding sufficient standard iron solution to make 0·5 gramme in every test. Thus the colouring matter in each series was identical in all the tests but varied in amount, while the iron and nitric acid remained constant. The results are shown in Fig. 5, curve B representing the former and curve A the latter series. It is clear that the results are strictly proportioned to the quantity of colouring matter present. Exactly similar results were obtained in the same way from quenched samples. A third series was made by using a solution of steel S to which excess of nitric acid equal to three times the amount in the Eggertz test had been added. The results are given in curve C, and they are again strictly proportional to the carbon present. These experiments prove, therefore, that the increase of colour due to iron is not reversible by dilution with water.

On reference to Table I. it will be seen that the colour-carbons of the majority of the steels, with carbons ranging from 0·17 to 2·35 per cent., are, in fact, proportional to the true carbon content when tested against the same standard. A few differences occur, but the above tests make it evident that such differences cannot be assigned to varying dilution of the tests.

Dilution with Nitric Acid.—Nitric acid solutions of the brown substance A, the colour of which has been increased by the addition of iron, are not appreciably altered in colour-value by dilution with nitric acid (1·2) instead of water; the tints, however, become greener.

The action of nitric acid on solutions of the green substance B was found to depend on the form in which the iron had been added to the solution. If the colour has been increased by the addition of iron *as standard solution*, the colour-value is only slightly diminished by dilution with nitric acid. This effect is shown in curve B, Fig. 6, which expresses the colour-ratio between two equal iron solutions of the colouring matter B, one of which has been diluted with increasing amounts of nitric acid and the other with water to match.

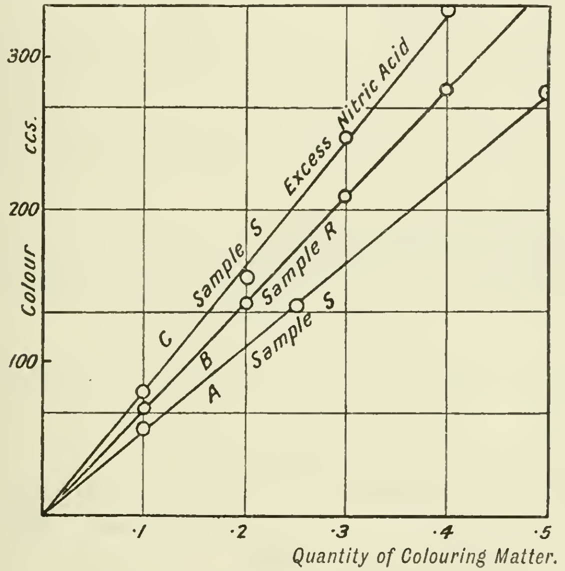

Fig. 5.—Influence of Dilution on Eggertz Results.

An entirely different result is produced when the same experiment is made on a solution of B to which iron has been added *as metal.* In this case the dilution with nitric acid causes a marked reduction in the amount of colour when compared with an equal quantity diluted with water. This effect is shown in curve C, Fig. 11. In both cases the addition of nitric acid causes the tint to become greener. A direct comparison was now made between two equal volumes of the green substance B to which iron had been added in the two forms. The solutions were diluted to match and their volume-ratio observed. Equal amounts of nitric acid were added to each and the colours again matched by dilution with water. The ratios obtained on successive additions of nitric acid are shown in curve A, Fig. 6. The addition of even a small amount (5 cubic centimetres) of nitric acid (1·2) was sufficient to remove the greater part of the "excess colour"[1] due to adding the iron as metal (see curves B_1, B_2, Fig. 4), while 5 cubic centimetres of strong nitric acid caused the colour-intensity of the two solutions to become almost the same.

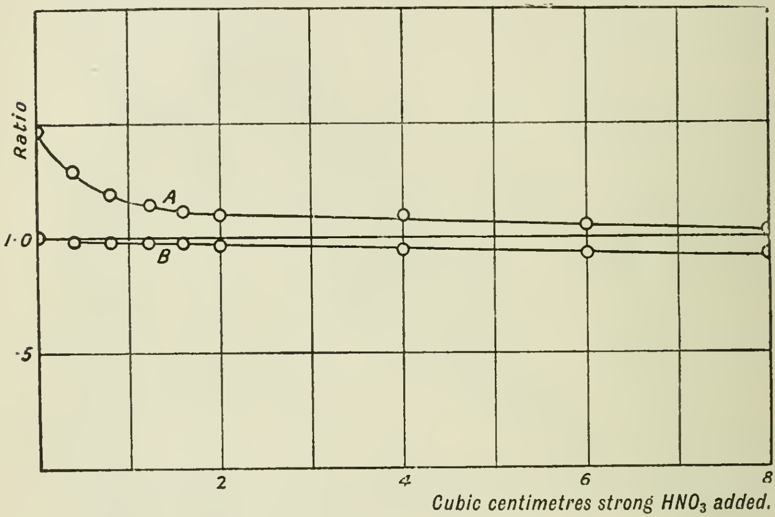

FIG. 6.

In all the preceding experiments, the ratio of iron to nitric acid in the standard solution used was the same as that in the Eggertz test (p. 31). When the standard solution contains a higher proportion of iron, the increase of colour and change of tint on mixing with solutions of substance B become still more marked; unlike that due to the action of metallic iron, this excess colour is not removed by the addition of nitric acid, although the tint, as usual, becomes greener.

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[1] This term will be used to indicate the colour removable by nitric acid.

Thus the green substance B exhibits two types of reaction with iron which are readily distinguished by the effect of subsequent additions of nitric acid. The one results from the addition of iron as nitrate, and the colour thus formed is only very slightly reduced in quantity by dilution with nitric acid. This reaction is, therefore, irreversible under such conditions. The other reaction appears only when metallic iron is dissolved in the solution of the colouring matter, and the " excess colour " formed in this case is removable by the addition of nitric acid. This reaction is therefore partly reversible.

Action of Heat.—It was observed that the lower the temperature during the solution of the metallic iron in substance B, the greater was the " excess colour " produced. The effect of heat on this " excess colour " was therefore next examined and, to estimate the amount present after heating, use was made of the ease with which it is removed by addition of nitric acid.

A solution prepared by dissolving metallic iron in an acid solution of substance B was boiled for a few hours in a reflux boiling flask. Two portions of 5 cubic centimetres were then removed and to one was added 5 cubic centimetres nitric acid (1·2); on dilution and comparison with the other, it was found that nitric acid additions still caused a reduction in colour-value. It seems, therefore, that the " excess colour " is not removed by boiling to the same degree as by the addition of nitric acid.

Influence of Hydrolysis on the Tint.—It has been repeatedly observed that, when nitric acid is added to a solution of compounds A or B containing iron, the tint changes and becomes gradually greener with increasing additions and, except when the " excess colour " is present, the colour-intensity is only very slightly lowered. It is also interesting to note in this connection that when solutions of substances A or B containing iron are diluted with water to about one-sixth the Eggertz strength and heated for two to three hours at 100° C., the tint slowly becomes redder, and it will be shown later that the colour-intensity is at first increased. These reactions, if considered from the standpoint of adsorption, suggest that the iron which is held by the colouring matter exists partly as hydrate and partly as nitrate. The amount of red colour in a given solution will thus depend upon the extent to which the iron is hydrolysed as well as upon the quantity of substance A present, and the slight changes in colour-intensity noted above will be due to the different colour-values of the iron as hydrate and nitrate.

With regard to the reversibility of the reactions caused by the addition of iron to the substance B, it must be admitted that no final explanation has been reached. In the first place, the change in tint and colour-value on addition of more nitric acid is instantaneous, yet the colour-intensity at first obtained depends upon the form in which the iron has been added. Again, when water is added to a test so as to reduce the concentration to that corresponding with the early part of the curve B_2, Fig. 4, the colouring power is not reduced ; the reaction thus appears irreversible. On the other hand, when two equal quantities of the green substance B are treated with equal amounts of standard iron solution, that added to one being concentrated and to the other diluted, then, on diluting the former to match the latter, their volumes are identical, a result which apparently implies reversibility of reaction between the iron solution and the colouring matter.

Much further work seems necessary before any clear explanation of those results can be expected. The problems belong to the spheres of organic and colloid chemistry, and the investigations here recorded were chiefly designed to provide data for comparing the Eggertz results given by variously treated steels.

RATES OF DECAY OF THE COLOURS IN THE EGGERTZ TEST SOLUTION.

The colour of the Eggertz test is well known to diminish on boiling. To examine the course of this decay, series of experiments were made in which the decay-curves were ascertained both for normal and quenched steels and for the separated colouring matters A and B. The effect of temperature on the decay of filtrates from quenched and normal steels has also been examined.

The first series of curves, showing the rates of colour-decay in the ordinary Eggertz method, was obtained by making up a number of similar tests of the same samples and placing them together in boiling water. A few drops of water were added to each from time to time to make up for loss by evaporation. The tubes were removed at intervals, cooled, and put aside in a dark place. When the last tube was removed, the colour-values were found by taking an intermediate test as standard so as to avoid any wide contrast in tint, because, as the boiling is prolonged, the colour becomes progressively greener due to the gradual change of the brown compound A to the green substance B by the action of the nitric acid. The results obtained in this way on samples A, E, F, N, are plotted in the decay-curves, Fig. 7.

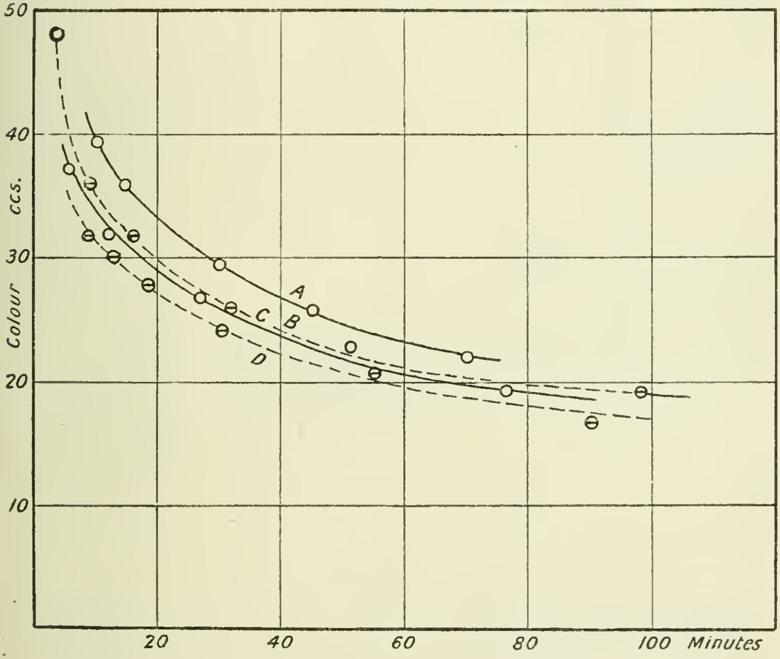

Fig. 7.—Decay in Open Tubes at 100° C.

Curve A.	Sample E.	Curve C.	Sample F × $\frac{1}{2}$.
,, B.	,, A × 2.	,, D.	,, N × $\frac{1}{5}$.

These curves indicate the approximate rates of decay in open test tubes and, to facilitate the comparison, the values given by steels differing greatly in carbon content were multiplied by factors, so as to bring the curves near together.

Owing to the uncertainty introduced by the evaporation, which takes place during the boiling when using open tubes, more accurate tests were made by dissolving 3 grammes of the sample in 60 cubic centimetres of nitric acid (1·2) and placing the solution in a 60 cubic centimetre flask fitted with a reflux tube. The flask was placed in boiling water and 5 cubic centimetre portions were removed with a pipette at suitable intervals. These were put aside and tested as already described. The results obtained by this method on both normal and quenched steels are plotted in Fig. 8. The numbers on the curves refer to the tints of the solutions when compared with the standard tint series. It will be observed that in the later stages the decay is not so rapid as when open tubes are used. The decay-curves for steels of varying

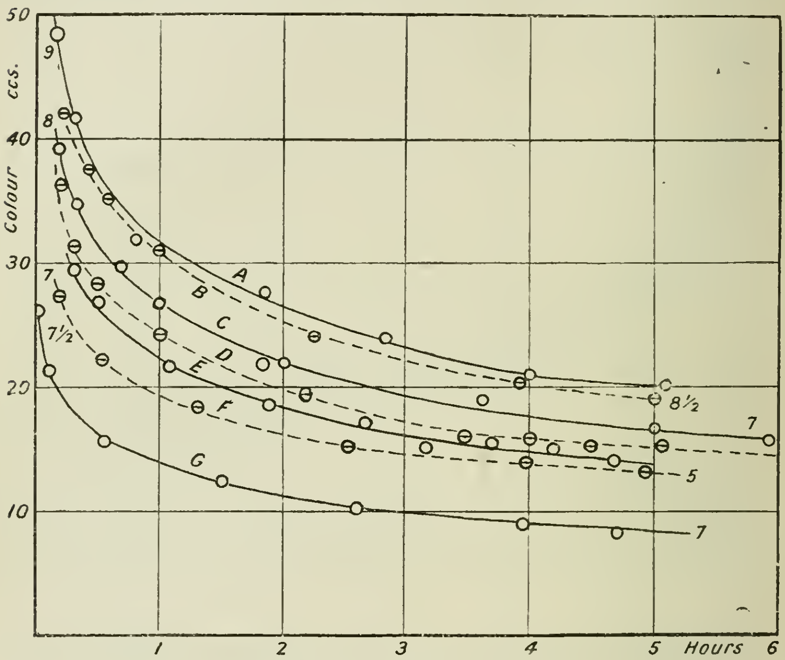

Fig. 8.—Decay Curves in Reflex Condenser at 100° C.

Curve A. Austenite. Sample R × $\frac{2}{3}$.
,, B. Annealed. ,, E.
,, C. Normal. ,, N × $\frac{1}{2}$.
,, D. ,, ,, F.
Curve E. Normal. Sample M × $\frac{2}{5}$.
,, F. Brown precipitate in 1·2 acid.
,, G. Quenched sample N × $\frac{1}{2}$.

carbon content are closely parallel, so that the Eggertz test could be made even after five hours' boiling. The colour-ratio between two similar solutions differing in concentration of colouring matter is thus independent of the time of boiling, and remains simply proportional to the concentration. It is therefore quite legitimate to multiply all values on such a decay-curve by a constant to facilitate comparison with curves obtained from other steels; much use has been made of this expedient in a later experiment.

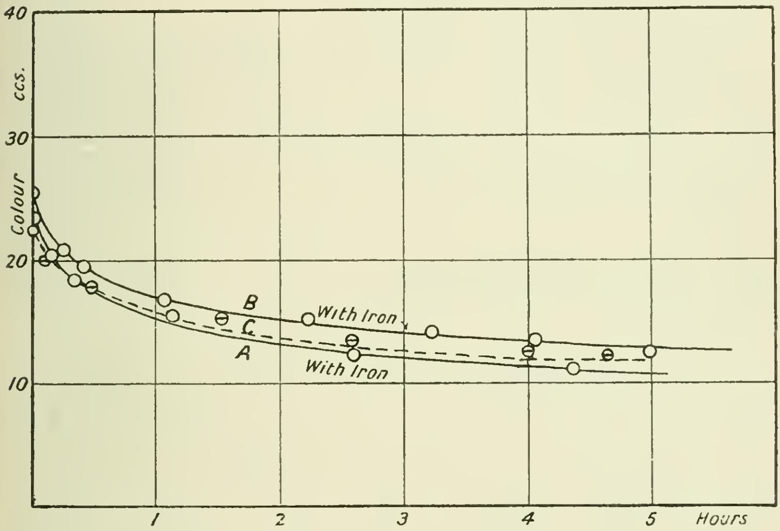

Fig. 9.—Decay of Coloured Compounds in Acid.

The decay-curves of the solution of the brown substance A and green diffusion B, which are obtained by dialysis, are given in Fig. 9. In preparing these solutions, the solutions of colouring matters were first made to 1·2 sp. gr. with nitric acid and then the correct amount of iron was added as metal (*i.e.* 0·5 gramme in each 10 cubic centimetres). Curve A refers to the brown precipitate A; curve B to the green diffusion B, which had been concentrated by boiling before the addition of the nitric acid and iron. Curve C shows the decay of the green compound in nitric acid (1·2) without the addition of iron; in this case the solution had not previously been concentrated so that any decay from this cause was avoided. Iron could not be added because, when the test was sufficiently dilute to be free from iron-colour, the colour-intensity was too weak for accurate matching.

The decay-curves for the two compounds lie very close together. The presence of varying amounts of the two substances in different steel solutions will therefore have very little effect on the decay-curves. It has been shown that the brown substance A slowly changes to the green substance B when boiled in nitric acid. The values on the curve A are therefore the sum of those due to the residual brown colouring matter A and the accumulating decay-products, especially the green body B.

Owing to the fact that the brown precipitate in a normal steel test dissolves slowly and the formation of the coloured solution is thereby retarded, a proper comparison with quenched steels, which dissolve to a complete solution very quickly, cannot be made. On reference to Fig. 8 it will be seen, however, that the initial rate of decay of normal samples is rather more rapid than that of quenched samples. It seemed advisable, therefore, to separate the precipitate and compare the filtrates only in this manner. For this purpose 3 gramme portions of steel N, in the normal and quenched condition, were dissolved in 60 cubic centimetres of nitric acid (1·2) without boiling. The solutions of both were filtered as quickly as possible, placed in the reflux flasks and their decay-curves ascertained at 100° C. In the same way, the decay-curves of similar filtrates at 71° C., 54° C., 33° C., and 18° C. were also found. Since the liquids became rather warm during the time the sample was dissolving, about 40 per cent. of the colour given by the normal steel was obtained in the filtrate, and the greater part of this must have been formed by the solution of the cementite. More than 90 per cent. of the colour given by the quenched sample was present in the filtrate, and the tint was only a shade greener than that given by the filtrate from the normal sample. The results are plotted in Fig. 10, in which the curves have been multiplied by factors to make them comparable (p. 53).

The rate of decay at the higher temperatures is at first very rapid in both cases, and any slight variation in time or other conditions of preparation would thus cause a considerable difference in the depth of colour of the filtrate. To avoid this inequality, which is very marked in the first few minutes, a separate experiment was made in which equal portions of the two filtrates were heated for one hour at the respective temperatures and compared against one test taken as standard. Since the filtrates given by the quenched and normal steel were not equal in colour-value, the two sets of results were each multiplied by the factor necessary to reduce the test at 18° C. to an arbitrary value of 50 cubic centimetres. These calculated values are plotted on the vertical line at time one hour in Fig. 10. The decay-curves at the different temperatures were now multiplied by the factors necessary to cause them to pass through the respective points on the line, and are so plotted in the diagram.

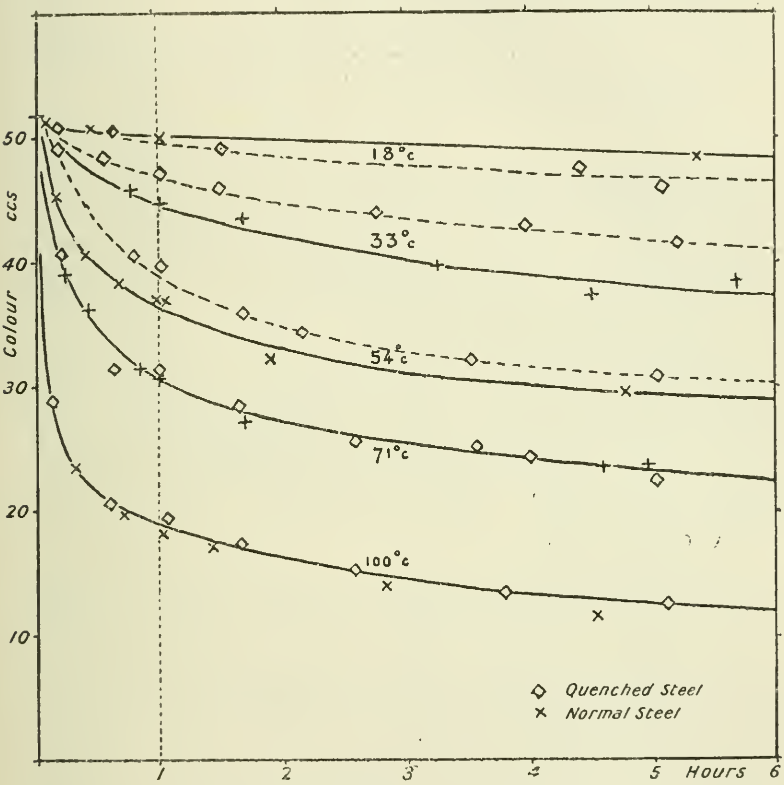

FIG. 10.—Effect of Temperature on Decay-Curves.

In this way a fairer basis of comparison was obtained than would have been got by equalising the values at time 0.

In spite of slight differences at lower temperatures, the general course of the curves given by the sample in the two conditions is remarkably close, and it is clear that as the temperature falls both reactions are retarded in the same way.

The Comparison of the Green Colouring Compounds in the Tests from Normal and Quenched Steels.

Owing to the fact that very little precipitate is formed when a quenched steel is dissolved in nitric acid (1·2), and that the solution cannot be dialysed satisfactorily in the presence of a large amount of iron, it was not found possible to isolate the green colouring substance given by quenched steels in the Eggertz test. The results of the preceding tests given in Fig. 10, the fact that solutions of both normal and quenched steels behave in precisely the same way when dialysed through parchments (p. 39), and that both give equally increased colour-values when extra iron has been added before dissolving (Table XVIII.), all suggest that the green colouring matters present in the two solutions are identical. Further evidence can now be given in support of this view.

1. When nitric acid is added to a test of either a normal or a quenched sample, the colour-value immediately falls in exactly the same way as when the addition of nitric acid is made to a solution of the green substance B in which metallic iron has been dissolved (p. 47). The effect of increasing additions of nitric acid to the tests from quenched and normal steels is shown in Fig. 11. Here 1 gramme samples high in carbon were dissolved in 20 cubic centimetres of nitric acid (1·2), boiled fifteen minutes, and diluted to 30 cubic centimetres with water. Several 5 cubic centimetre portions were taken and nitric acid (1·2) was added to the different tubes in amounts varying from 1·0 to 30 cubic centimetres. The colour-values of the tests were then measured by diluting them to match the portion containing no extra acid. Curve A was given by a normal steel, curve B by a quenched steel, and curve C by a solution of the green substance B in which metallic iron had been dissolved so as to give the Eggertz test

concentration. In the case of curves B and C much less colouring matter was present in the solutions than in that giving curve A, and the addition of nitric acid to the tests could not be carried so far before the iron-colour disturbed the result. It is quite clear, however, that in all cases the addition of nitric acid has the same effect, the loss of the "excess colour" being the most marked at the beginning. Thus the green substance, as it is formed in solutions of both quenched and normal steels, takes up iron in a similar way to substance B when the iron is dissolved in its nitric acid solution.

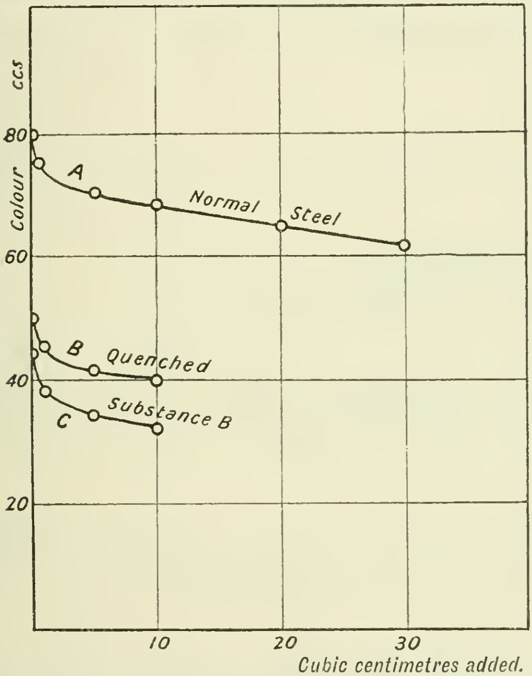

FIG. 11.—Removal of "Excess Colour" by addition of Nitric Acid (1·2).

2. It has been previously shown that the "excess colour" given by substance B is not destroyed through prolonged heating (p. 49). By taking decay-curves of normal and quenched samples and comparing two 5 cubic centimetre portions of the solution at intervals, adding 5 cubic centimetres of nitric acid (1·2) to one of

them, it can be demonstrated that the " excess colour " present in each case is likewise not removed by heating. Curves A, B, Fig. 12, were so obtained, A being given by a normal steel and B by a quenched; the lower line indicates the colour-value of the test after the addition of the nitric acid. It will be observed that the ratio of the reduction in colour-value to the amount present is not altered in either case even after five hours' boiling. This fact again strongly indicates that the green colouring matters are the same, and must also be regarded as distinct evidence that the colour-decay, which takes place on boiling both normal and quenched samples, is not even partially due to the removal of any iron from the green colouring substance.

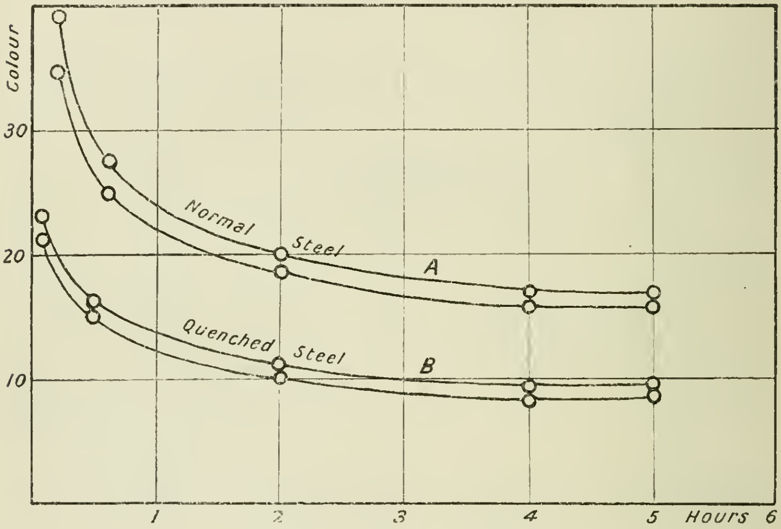

FIG. 12.—" Excess Colour " during Decay.

3. It was repeatedly found that, on boiling dilute solutions of both quenched and normal steels for two hours or more, the colours became much redder, the tints rising two to three values on the standard tint series (p. 32). The results shown in curve A, Fig. 13, were obtained by dissolving 0·5 gramme portions of sample R, in the quenched and in the normal state, in 10 cubic centimetres of nitric acid (1·2), boiling each fifteen minutes and diluting to 50

cubic centimetres with water. The heating was then continued and the decay-curves taken as usual.

The dotted circles on the curve indicate the colour-values given by the normal steel, and it will be observed that in this case the colour-value actually rose slightly at first, and in the other (the quenched steel) it remained stationary for a while. The effect of the normal decay which is taking place is, therefore, counteracted in both instances by a reaction which causes an increase and reddening of the colour. This reaction has also been shown to occur in dilute solutions of the dialysed substances A and B, and as already indicated (p. 49) is most probably due to the hydrolysis of the iron compounds linked with the colouring matter.

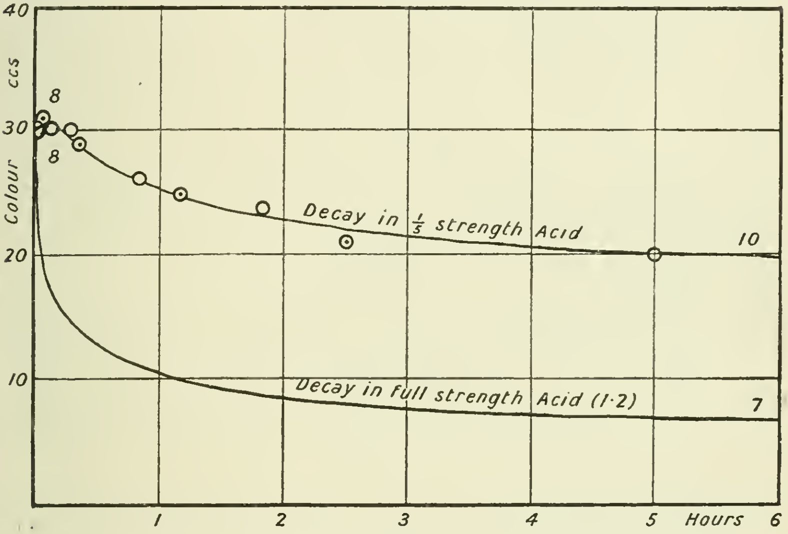

FIG. 13.—Influence of Acid Strength on Decay. Lower curve taken from Fig. 10 for comparison.

4. The various effects of the addition of nitric acid and iron to the solutions are well illustrated by the following experiment. One gramme of sample S was dissolved in the usual way and boiled for fifteen minutes; the test was then diluted to 100 cubic centimetres with nitric acid (1·2). A solution was thus obtained in which the ratio of iron to nitric acid was greatly diminished. The

decay-curve of this solution is shown as the lower curve in Fig. 14. After five hours' boiling the colour of the test had become greener (tint 7). The ordinary decay-curve which would have been obtained had the solution not been diluted with nitric acid is indicated by the broken line. The rate of change is at first much increased by the additional nitric acid, but afterwards the two curves become parallel.

After the five hours' boil 2 grammes of metallic iron were dissolved in 50 cubic centimetres of the solution ; the ratio of iron to nitric acid was thus brought again to that of the Eggertz test. The colour increased by about 100 per cent., as indicated in the curve, and the tint became decidedly redder, the exact increase and change of tint being found to depend upon the temperature of the solution while the iron was dissolving. From this it would seem that the green tint which results from boiling five hours with the excess of nitric acid is due to the removal of iron from the colouring matter as well as to the transition of the brown to the green compound.

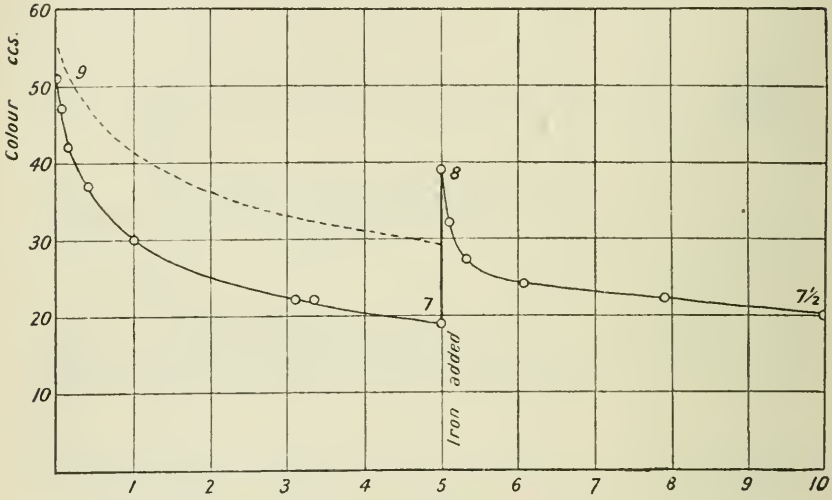

FIG. 14.

Addition of nitric acid to this solution after the iron has dissolved, removes most of the "excess colour" in the cold at once, but there remains the more permanent iron-coloration

(p. 48). A decay-curve at 100° C. was now taken after the addition of the iron. The colour-value fell very rapidly during the first hour, as shown in Fig. 14, then quite slowly, the final rate of decay being such as would be expected from a test which had been boiled for nearly ten hours. This decay may probably be regarded as due to the slow destruction of the colouring matter, while the quick drop in the first stages after adding iron is due chiefly to the loss of the greater part of the "excess colour," which was formed in large quantity as indicated by the effect of nitric acid additions.

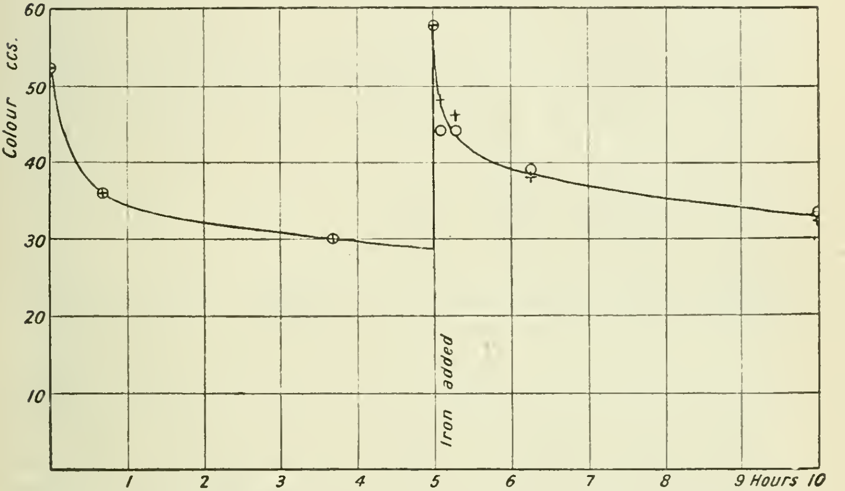

Fig. 15.—Results from Normal Steels are shown by Circles, Quenched Steels by Crosses.

For the comparison of quenched and normal steel tests when treated in this way, two samples were chosen so that the colour-carbon given by the normal sample of the one was the same as that given by the quenched sample of the other. One gramme portions of each were carried through the procedure which has just been described, and yielded the results shown in the curve, Fig. 15. Since the colour-values of both steels were the same and each test was diluted to the same extent in the experiments, the comparison of the results is not affected by any error due to iron-colour. The two curves coincide throughout their course. The tints, however, at the beginning were widely different ; after the addition of nitric acid and boiling for about two hours they became the same and remained so throughout, except immediately after the iron had been added, when the quenched test appeared to be slightly greener. This experiment of itself places the identity of the green colouring matters in the solutions of quenched and normal steels almost beyond doubt.

5. In taking the ordinary decay-curves of normal and quenched samples of the same steel, it was observed that the colours of the two gradually became the same when compared on dilution. The time required to effect this, however, varies according to the size of the carbide in the normal sample ; five hours' heating was sufficient in the case of steel N (photo. 1), but nearly fifteen hours was required before the tint of the normal sample of steel R (photo. 5) became the same as that of the quenched sample. As the heating is further prolonged, the tints of the two still keep the same, becoming slowly greener, and on boiling for twenty-four hours they were found to have dropped to between tints 6 and 5 of the tint series. The possible explanations of this gradually changing tint need not be discussed here ; the important feature is that, when the brown substance A in normal steel solutions has changed to the green substance B, the colour exactly matches and continues to match the colour of a quenched steel test made under similar conditions, and it seems reasonable to conclude that the same substances are present in both cases.

6. When solutions of the brown precipitates, given by both normal and quenched steels on dissolving in very weak nitric acid, are dialysed, the results obtained furnish additional evidence which points to the same conclusion. Three gramme portions of sample R, in the quenched and normal state, were each allowed to dissolve in the cold in 250 cubic centimetres of a solution containing 25 cubic centimetres of strong nitric acid. The liquids were then filtered, and the precipitates, after washing, were dissolved by boiling them for about thirty minutes in 20 cubic centimetres of nitric acid (1:2) ; the solutions so obtained were dialysed in collodion bags as previously described. In each case a large amount of a green compound passed through the membrane into

the surrounding water; no brown precipitate was thrown down in the bag containing the solution of the quenched steel precipitate and only a slight quantity in that holding the normal precipitate. On testing the green diffusions, the reactions of each with ammonia and with additions of iron solution, &c., were found to be exactly the same as those given by the green solution B previously described, and the conclusion was arrived at that the three substances are one and the same compound.

To sum up, therefore, it must be admitted that the foregoing experiments indicate very strongly that the green colouring matter in the Eggertz test solution of a quenched steel differs in no essential respect from that derived from the brown substance which is formed when a normal steel is dissolved in acid of the same strength.

V. The Colourless Products in the Solution.

The fact has long been known that quenched samples give a much lower colour-value than annealed steels, and that samples in intermediate conditions yield intermediate results. It has already been proved in Part II. that this "missing carbon" of quenched steels is to be found in the solution and does not escape as a gas. Since previous experiments have shown that the same ratio of "excess colour" is removed by the addition of nitric acid to the tests of normal and of quenched steels (p. 57), the lower colour-values of the latter cannot be due to any lack of coloration by the iron, and therefore must be the result of the formation, at an early stage, of a colourless or only slightly coloured compound (or compounds).

The rate of the evolution of carbon dioxide from this colourless substance during the boiling can be approximately determined in the following manner. The figures under column 1 in Table XIX. are based on results given in Part II., and from these it will be seen that after six hours' heating the solution of both quenched and normal steels retains a little over 40 per cent. of the original carbon in the sample, since this had not been evolved in the gases. To confirm this indirect result, direct experimental evidence was obtained as follows: 2·5 grammes of the samples J and N (quenched) were each dissolved in 50 cubic centimetres of nitric acid (1·2), and after the solutions had been boiled for ten minutes in reflux flasks, 5 cubic centimetre portions were withdrawn and colour-tested. The heating was then continued for six hours and the colours again compared in the same way. It was found, as usual, that the two colour-values were still in the same proportion, and also that the tints of the solutions had become the same (tint 7). The remaining 40 cubic centimetres of each was placed in the special apparatus A, B, Fig. 2, and treated with a solution of potassium permanganate as described in Section IX., Part II. The amount of the carbon oxidised to carbonic acid was found by absorption in the ammoniacal barium chloride solution. As the whole of the carbon is not oxidised by this means (see Table XVII.), the value obtained was increased by the correction required to give the full amount. The results agreed quite closely with those arrived at by testing the evolved gases, and they are given in Table XIX. under columns 2 and 3.

Table XIX.—*The Amount of Carbon in the Solution after Six Hours' Boiling.*

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	1. Approx. per Cent. of the Carbon Evolved as Gas in 6 Hrs. (Part II.).	2. Amount of Carbon per Cent. found by Use of $KMnO_4$.	3. Per Cent. of the Carbon left in the Solution after 6 Hours.
J	Normal	0·54	58·5	0·21	39·0
N	Quenched	0·78	58·0	0·286	37·0

Now the solution of the quenched steel N contained a much greater proportion of the colourless product than that of the normal steel J. If this product evolved carbon dioxide, in proportion to its carbon content, at a different rate from the green substance present in both solutions, a greater proportion of carbon dioxide should have been liberated from one solution than from the other. (The solution of the normal steel also contained, at first, a certain amount of the brown compound A, but it has already been shown that the rate of evolution of carbon dioxide from a steel yielding principally this body is the same as that from other steels (see Table III., sample E).) On reference to Tables XVII. and XIX.

it will be seen that the proportion of carbon remaining in the solution of the normal steel is practically the same as that in the quenched steel solution both after ten minutes' and six hours' boiling; as the colour-ratios remained the same throughout, the rate of evolution of the carbon from the colourless product in the quenched steel test must, therefore, be approximately the same as that from the brown and green substances. (See Table VI.)

There is at present no means of determining how much of the carbon in the solution is contained in the colouring matter, With quenched steels it is probably much less than half, for it can be shown that colourless products are also present at an early stage in normal steel solutions. One gramme portions of samples G and N were dissolved in 20 cubic centimetres of nitric acid (1·2) in the cold and heated for about five minutes at 50° C. The brown precipitate was filtered off, in each instance, on to an ignited asbestos felt contained in a small Gooch crucible. The filtrate was put on one side, and after the precipitate had been washed with water the crucible was placed in the combustion tube and the carbon in the precipitate found by combustion as described in Part I. Ten cubic centimetres was withdrawn from the filtrate and, after boiling ten minutes, was colour-tested against a 0·5 gramme portion of the same steel which had been similarly treated. The results are given in the following table:

TABLE XX.

Sample.	Carbon per Cent. in Sample.	Carbon per Cent. in Precipitate and Lost as Gas.	Carbon per Cent. in Filtrate by Difference.	Colour-Carbon per Cent. in Filtrate.	Ratio of Colour-Carbon.	
					Steel.	Filtrate.
G	0·42	0·23	0·19	0·11	1·0	0·59
N	0·78	0·42	0·36	0·24	1·0	0·67

Thus, these filtrates must have contained colourless products. On reference to Table VII. it will be seen that the amounts of carbon dioxide liberated from a similar filtrate and precipitate from sample N were the same. The colourless products present in the solutions of these normal steels are, therefore, attacked by the nitric acid, with the liberation of carbon dioxide, at much the same rate as the coloured substances are attacked. This deduction is well supported by the fact that all steels were found to yield, on heating, the same proportion of their carbon as carbon dioxide, irrespective of their colour-values, the only feasible explanation of which appears to be that the gas is given off by the brown, green, and colourless products at the same rates.

In this connection mention may be made, in passing, of the fact that when the dialysed brown precipitate obtained from a solution of the precipitate given by sample N was dissolved in nitric acid containing iron in the proportions of the Eggertz test, and boiled for thirty minutes, it only gave one-half the amount of carbon dioxide which would have been obtained from a quantity of the steel giving the same colour-value as the solution. The preparation for the dialysis was made by boiling the precipitate for ten minutes in nitric acid (1·2) and filtering. This experiment would seem to indicate that about one-half the carbon dioxide given off by normal steels is derived from colourless substances. Several attempts were also made to find the amount of carbon dioxide yielded by the green diffusion B under similar treatment. It was found to liberate much more of the gas in proportion to its colour-value than the brown substance, as might be expected if colourless products are also present in the diffusion. Unfortunately the experiments were not conclusive, because dilute nitric acid appears to have a solvent action on both parchment paper and the collodion bags, for on subsequently heating the acid in which the membrane had been soaked some carbon dioxide was liberated.

The Conversion of the Green Substance to a Colourless Body.— The ratio of the colour-value to the carbon content of the test solution of both quenched and normal samples diminishes as the boiling is continued. The results of a number of separate experiments have been collected in Table XXI. to demonstrate this point. The figures in column A have been derived from Table XVII.; those in column B were obtained by testing the gases liberated in the interval between ten and forty minutes and comparing the colour-values of the solution at ten minutes and forty minutes; the method of arriving at the figures in column C has already been stated in connection with Table XIX.

TABLE XXI.—*Showing the Diminishing Ratio of Colour to Carbon in the Solution.*

Sample.	Condition of Sample.	Carbon per Cent. Sample.	A. 10 Minutes' Boil.			B.[1] 40 Minutes' Boil.			C.[2] 6 Hours' Boil.		
			Colour-Value.	Carbon per Cent. in Solution.	Ratio.	Colour-Value.	Carbon per Cent. in Solution.	Ratio.	Colour-Value.	Carbon per Cent. in Solution.	Ratio.
J	Normal	0·54	0·54	0·39	1·38	0·39	0·31	1·26	0·21	0·21	1·0
,,	Quenched	,,	0·345	0·39	0·88	0·255	0·32	0·80	...	...	...
N	Normal	0·78	0·78[3]	0·545	1·43	0·57	0·44	1·29	0·31	0·30	1·0
,,	Quenched	,,	0·50[4]	0·545	0·91	...	...	...	0·20	0·29	0·69

The differences between the fall in colour-value and in carbon content of the solutions of sample N are also shown in Fig. 16 (p. 68), the curves of which have been plotted from the values given in the above table.

That this difference is not due to the removal of iron from the green substance has already been shown (p. 58), and seeing that the colourless products evolve carbon dioxide at about the same rate, in proportion to their carbon content, as the coloured bodies, it seems clear that the green colouring matter formed on dissolving, or subsequently formed from the brown compound, besides being directly oxidised to carbon dioxide, is also being slowly transformed into a colourless or only slightly coloured substance by the action of the nitric acid.

VI. THE INFLUENCE OF SIZE OF CARBIDE PARTICLES ON THE EGGERTZ TEST RESULTS.

The decay-curves in Fig. 10 clearly indicate that at higher temperatures the fall in the colour-value of the test solution is very rapid during the first few minutes, and thus the necessity of dissolving the standard and sample at the same temperature, and under exactly equal conditions, is at once evident. If, in dissolving, one test should attain a higher temperature than the other, the additional decay which results may be sufficient to cause an error. To demonstrate this, three 0·5 gramme portions were taken of a sample, in which the carbide was not too coarse, and each was dissolved in 10 cubic centimetres of nitric acid (1·2), the first by constant shaking under the tap, the second without being cooled, so that its temperature rose to about 60° C., and the third by placing the large tube containing the drillings into boiling water immediately after the addition of the acid: As soon as the reaction in the last case had subsided, the other two tests were also placed in the water and all three were boiled

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[1] Both colour and carbon values in this column refer to decay while air was passing through the apparatus.

[2] These values refer to decay in reflux boiling flasks.

[3] Taken as standard.

[4] Sample not completely quenched.

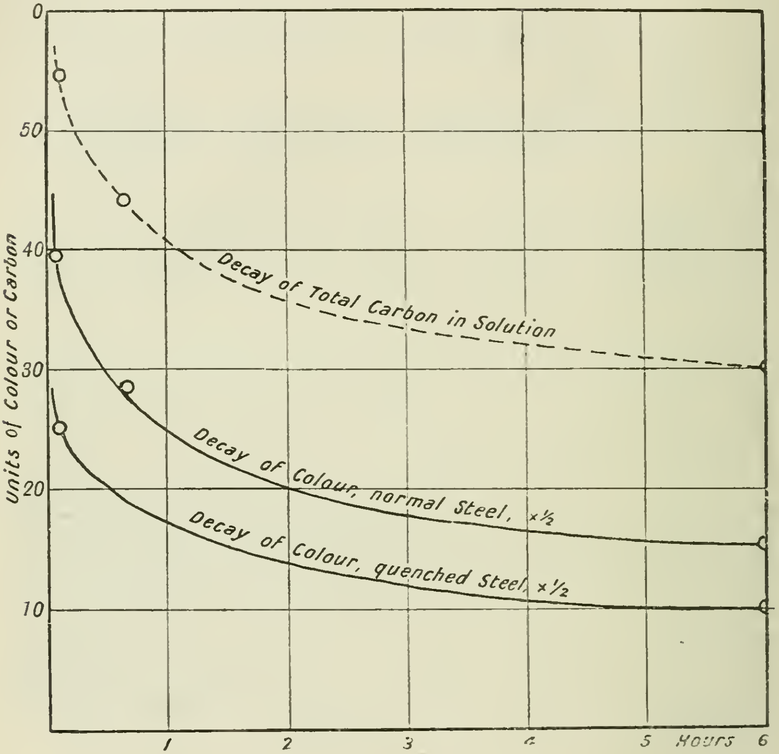

FIG. 16.—Colour Curves from Fig. 8.

for the same period of time (usually fifteen to twenty minutes). They were then cooled and their colours matched, the first being taken as standard. This experiment was made with several such steels, and the results are given in the upper part of Table XXII. It will be seen that in each case the sample dissolved in the cold gave the highest colour-value.

Table XXII.

Sample.	Condition of Sample.	Carbon per Cent. in Sample.	Colour Test. T° of Solution while Sample Dissolved.		
			10° C.	60° C.	100° C.
F	Normal	0·38	0·38	0·36	0·355
G	Quenched	0·42	0·29	0·27	0·26
J	Normal	0·54	0·54	0·50	0·50
N	,,	0·78	0·78	0·72	0·71
E	Normal	0·37	0·37	0·38	0·42
R	,,	1·40	1·40	1·46	1·65

On similarly testing samples containing coarse carbide particles quite another effect was obtained. Here, on dissolving at 100° C., instead of a decrease, there is a very marked increase in colour-value, as shown in the lower part of Table XXII., and the brown precipitate formed under such conditions is much slower in dissolving in the acid; in fact, it sometimes requires thirty minutes to effect a complete solution.

The increased colour produced by dissolving at 100° C. occurs only with the coarser precipitates, the particles of which do not swell to any great extent when formed (p. 36). This more compact type must be much less hydrated than the transparent swollen particles, and consequently less exposed to the solvent action of the acid. Many colloids are precipitated in a less hydrated form under the influence of increased temperature; that this is a property of the brown precipitate is shown by the fact that, when it is boiled in water in a glass beaker, the brown substance is sometimes precipitated as a coherent film on the bottom of the vessel; this film is most resistant to the action of nitric acid, and a similar effect may well occur at the surface of the less hydrated large particles at 100° C.

The less hydrated particles formed from coarse carbide have been shown to retain their iron content longer, and the hardening effect at 100° C. may be associated with a "tanning" action through which the iron becomes more firmly held by the colloid. The fact that the colour of the test dissolved at 100° C. is usually redder on dilution than the ordinary test lends some support to this view, the presence of additional iron causing, as in other cases mentioned, a redder tint.

The Solution of Annealed Steels.—A test of a thoroughly annealed steel yields compact large particles of precipitate on dissolving in the cold. When such a test is placed in boiling water, a hardening action, similar to that described above, seems to occur to some extent, as the time required to obtain a clear solution is longer than with normalised samples containing very fine pearlite. The colour-values of these well-annealed steels are too high when compared with an air-cooled steel as standard, and the tints are redder ; an explanation of these effects, which have long been observed, is to be sought not in any difference in the amount of carbon lost as gas, but in the delay which occurs in the solution of the precipitate, whereby the change brown—green—colourless is retarded. (See also remarks below on variations of tint in the Eggertz test.)

Two Causes of Variation in Colour-Value.—The above explanation will only account for the higher colour-values given by annealed steels; the wider difference between the tests from normal and quenched samples of the same steel must find its explanation chiefly in the early formation of the colourless product (p. 63), in the solution of the quenched sample. This last is the true "missing" carbon. In intermediate steels the total "missing" carbon defined by Howe[1] will be the sum of that due to diminishing delay in the solution of the precipitate as compared with the standard steel test and that due to the additional colourless product formed as in the quenched tests. Whatever the source of the colourless product, it is evident that only this part of the total "missing" carbon represents the real difference between quenched and annealed steels. The delay arising from the size of the carbide particles is an accidental effect of the properties of the colloid colouring-matter.

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[1] *Journal of the Iron and Steel Institute*, 1895, No. II. p. 275.

Variations of Tint in the Eggertz Test.—The behaviour of the brown compound A in dialysis suggests that its solution in nitric acid is the result of a process resembling peptisation, and that the colloidal particles in the solution vary considerably in size; thus, on dialysing a solution of the precipitate, the largest particles are first thrown down as a coarse precipitate as the acid is removed, while the smallest are not precipitated even when the liquid becomes neutral, so that, on filtering, a brown filtrate is obtained (p. 41). It has been shown that this brown substance gradually changes to a green compound on boiling in nitric acid, and, as a rule, the slower the precipitate is in dissolving, the longer is the time required before the normal sample becomes as green as the quenched (p. 62); for instance, in the case of sample N five hours was sufficient, while samples E, R, S, with coarse carbide, required ten to fifteen hours. Thus the hardening of the coarse compact particles of the precipitates, which takes place in the boiling solution, not only makes them more resistant to the peptising action of the acid, but also retards the further change of the particles, when in colloidal solution, to the green substance, and this further delay also tends to raise the colour-value. For the same reason, the tint obtained after fifteen minutes' boiling varies with the size of the carbide particles. This effect is well seen in the tests given by a series of such pearlitic and annealed steels as samples M, N, G, A, C, R, and E, which yielded a gradation of colours between tints 8 and 10 of the tint series, becoming progressively redder in the order given. Sections of each steel were examined under the microscope and the carbide photographed after being stained with sodium picrate.

Sample M gave the greenest tint of all, though not quite so green as a thoroughly quenched steel; even under the highest magnification available it contained sorbitic areas in which the carbide structure could not be resolved and a photograph was not taken. The next in order of tint was sample N, which contained extremely fine pearlite, all of which could be distinguished, as seen in photo. 1. Sample G followed this, and its carbide is seen in photo. 2. Even in these cases the lines of carbide are so extremely thin that they have not been properly resolved by the oil immersion lens and appear greyish instead of black. It will be noticed in photo. 2 that there is a slight balling up of the cementite at the margins of the pearlite areas. This is still more pronounced in photo. 3, taken from sample A, which came next in order. A still browner tint was obtained from sample C, photo. 4, and it will be seen that its carbide is again decidedly coarser than the preceding; the colour of sample R, photo. 5, was intermediate between this and that of sample E, photo. 6, which gave the brownest tint of all.

This comparison makes it clear that, as the average size of the cementite particles increases, the tint of the test becomes browner, and this conclusion was confirmed by many tests of the same kind which were made on other samples. It follows that the presence in the steel of any element which tends to retard the growth of the carbide will cause the colour of the test to appear greener than that of another steel not containing any such element and having the same heat treatment. Manganese is an instance of this, and the series just described includes steels of widely differing manganese content, but that the essential cause of the variation in tint is really connected with the carbide size, and not with the chemical action of the manganese, was proved by thoroughly annealing at 680° C. the sample M, highest in manganese; the tint obtained from it was then as brown as that given by sample R, although the manganese content of the carbide could hardly have altered. It can also be shown that the presence of manganese nitrate in the solution has no direct influence on the colour by adding that compound to a test, when dissolving; the addition of considerable quantities has no effect whatever on the colour.

The objection may be raised that the fineness of the visible carbide is merely an index of the amount of invisible " hardening " carbon remaining in solution in the ferrite, and that the latter form of the carbon is the true source of the increasing greenness of tint and lower colour-values. (See Part IV., Table XXVIII.) The outstanding effect of this " hardening " carbon (*i.e.* of carbon as it exists in thoroughly quenched steels), is, however, the marked lowering it causes in the colour-value. Hence, if the green tint were solely due to the presence in the steel of " hardening " carbon this should also be indicated in the lower colour-value of the test, as in the following experiment: Two sections of sample N were taken, one was annealed for ten hours at 680° C. and the other quenched from 800° C. in water; the colour-values after this heat treatment when tested against the normal sample were 0·84 and 0·43 respectively. A test was made up of equal amounts (0·25 gramme) of these two samples and compared with a similar test (0·5 gramme) of the normal steel; on dilution, the tints were found to be an exact match. Now, if the green tint of the normal sample had been caused by the presence of "hardening" carbon, the colour-values of the two tests should also have been equal, whereas the mixture only gave a value of 0·66 against the 0·78 value of the normal sample. Such an experiment clearly shows that the green tints are not necessarily due to the presence of "hardening" carbon in the steel. Moreover, the sharply defined pearlite and initial stages of divorcing seen in photo. 2 are conditions which, of themselves, seem incompatible with the persistence of any appreciable amount of "hardening" carbon in the ferrite; yet the colour of this sample (G) was quite green when tested against a well-annealed steel.

The chief explanation of the varying tints in the series photographed must be sought in the rates of solution of the brown precipitates (p. 37) and in the retardation of the change from the brown substance A to the green compound B which results from the hardening at 100° C. of the precipitates from the coarser carbides. That, as the carbide becomes finer, the precipitate is more easily soluble, was shown by dissolving tests of samples E, C, G, and N in the cold and filtering. The filtrates were matched against a suitable standard and the volume of each divided by the carbon content of the steel. The results are given in the following table:

TABLE XXIII.

Sample.	Photo.	Colour-Values of Filtrates per Unit of Carbon in the Steel.
E	6	0·8
C	4	1·1
G	2	1·2
N	1	1·4

The Origin of the "Missing" Carbon.

As very little brown precipitate is given by quenched steels, when dissolved in nitric acid (1·2), the retardation of the colour-decay, due to the slow rate at which the precipitate dissolves, will not occur. The solution is nevertheless much browner in colour than after it has been heated to 100° C., the change to green rapidly taking place between 70° to 80° C. It is evident, therefore, that in both quenched and normal steel tests there is, to some extent at any rate, the same order of change in the colouring substances. The brown compound first formed is changed to a green substance, which appears to be identical in all cases, and this then slowly changes to the colourless product (p. 67). The rate of change from the brown to green in normal steel tests varies considerably, and depends to a large degree upon the size and condition of the component particles of the brown precipitate which is formed from the carbide particles (p. 71). Thus it is only to be expected that if the brown substance is formed from extremely divided carbide in quenched steels, it should change to the green at the quickest rate. Seeing that the amount and condition of the carbon in the gases evolved from both normal and quenched steels were found to be the same (Part II.), and that the colouring matters decay in the same manner and have so much in common, the question arose as to whether an acceleration of the reactions after dissolving owing to the extreme fineness of the carbide would be sufficient alone to account for the "missing" carbon. The differences observed in the tint and colour-value given by one steel in the two conditions might well be accounted for, as already explained, simply by the great difference in the size of the carbide particles causing the tests from quenched steels to be much further advanced through absence of "delay," in the order of change brown—green—colourless, than those from normal steels. This explanation of the differences, though attractive, is irreconcilable with the following facts and was therefore discarded.

1. The solutions obtained on dissolving quenched steels in the cold with the greatest care give a colour-value which is far too low to meet the requirements of the above explanation. On comparing the colour-value given by a test of a quenched sample

dissolved in the cold with that obtained from a similar test after boiling ten minutes, the difference found was not so much as that between the latter and an annealed sample of the same steel after it had been boiled for ten minutes. As the rate of colour-decay has been shown to be very rapid in the first ten minutes, it is evident that the quenched steel test when first dissolved must already have contained a considerable amount of the colourless products. The results of two such experiments are given in the following table :

TABLE XXIV.

	Sample M.	Sample P.
	Cubic Centimetres.	Cubic Centimetres.
Quenched test dissolved at 10° C. (not heated) . . .	60·0	75·0
,, ,, ,, boiled 10 min. . .	40·0	43·0
Annealed ,, ,, ,, ,, 10 ,, [1] . .	71·0	84·0

2. Two 1 gramme portions of sample N, in the quenched and normal conditions, were each dissolved in 80 cubic centimetres of weak nitric acid (1 : 9 aq. by vol.) in the cold. The colours of the filtered solutions on matching were exactly the same both in tint and quantity. On dissolving the precipitates in nitric acid (1·2) at 100° C. without the addition of any iron, and comparing the colour-values, the solution of the precipitate from the quenched sample was found to be much the lower, the ratio of the two being 27 : 42 ; on adding an equal amount of iron to each, the colour was increased but the ratio remained the same. As far as could be seen the two precipitates dissolved at the same rate, and about thirty minutes was required to effect a complete solution ; the lower colour-value given by the quenched steel precipitate could not, therefore, be due to any difference in the speed of the reactions in this case, so that true "missing" carbon was present in either the filtrate or precipitate from the quenched steel. It was next found, by oxidation with potassium permanganate, that the filtrate from the quenched sample contained considerably more carbon than that from the normal sample, and, as the colour-values of the filtrates were the same, it is again

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[1] Taken as standard.

evident that the colourless product or "missing" carbon of quenched steels is formed as the sample dissolves, and in the above experiment it was present chiefly in the filtrate.

Thus, while the results of the gas analysis given in Part II., and the marked similarity of the reactions of the colouring matters, both strongly indicate that cementite (Fe_3C) is still present in what appears to be solid solution in quenched steels, the early formation of excess of the colourless body might seem, on the other hand, to indicate that at least part of the carbon is present in another form. It has already been shown, however, that the character of the brown precipitate given by normal steels can vary with variations in the size of the carbide particles (p. 35). A further instance of the differences which can arise from a change in the conditions of solution was found in the behaviour of carbide separated from steel by electrolysis. A bar of a steel, from which the brown precipitate for the dialysis experiments had often been prepared, was treated by the method of electrolysis described by Arnold and Ibbotson,[1] and the adhering carbide removed and dried. On heating some of this preparation in nitric acid (1·2) at 100° C., the greater part gradually dissolved, but it was noticed that there was a residual quantity of the brown precipitate which was only dissolved with difficulty after long boiling. This effect was not observed in dissolving the steel. One gramme of the carbide was next boiled in 20 cubic centimetres of nitric acid (1·2) for fifteen minutes, filtered, and the solution dialysed. The surrounding water rapidly became coloured and, after standing for one day, the greater part of the colouring matter had been removed by the successive changes of water; there remained in the bag a small amount of the brown precipitate A, largely contaminated with ferric hydrate, and a lightly coloured solution. The diffusion also contained a large quantity of iron and was found to give the same reactions as substance B. The experiment clearly proved that, on dissolving carbide, out of contact with iron, in nitric acid, much less of the brown substance A was formed and much more of the diffusion B than when the carbide of the same steel was not first isolated.

The above observation at once suggested that the nature of the carbide reaction, when a steel is dissolved in nitric acid, might be influenced by the degree of electro-chemical action between the iron and the particles of carbide imbedded in it. So long as the particle remains in contact with the metallic iron it will form the pole of a minute cell, and in such a cell the current will flow from the iron to the carbide through the acid,[1] hydrogen being displaced toward the carbide surfaces while the NO_3 is concentrated at the iron which dissolves. In considering the difference in behaviour between large and fine carbide particles, account must therefore be taken of the length of time they, or their products, remain in contact with the iron and are exposed to these electro-chemical reactions before floating away into the solution, and also of any differences which may exist in the energy available on solution of the metal.

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[1] "Steel Works Analysis," p. 436.

In order to ascertain the effect on the colour-value of an intensification of the electro-chemical action, some experiments were made by dissolving steel samples in a small electrolytic cell, one pole of which consisted of a piece of platinum foil and the other of a rod (about $\frac{1}{8}$ inch square section) of the steel to be tested. The steel was connected with the carbon pole of three dry cells in series, the platinum to the zinc. 10 cubic centimetres of nitric acid (1·2) was placed in the cell and the current passed through the solution; an ammeter which was placed in the circuit registered 0·7 ampère. The reaction of the steel was greatly altered, almost no nitric oxides being evolved; much gas (presumably hydrogen) was given off from the platinum and also a steady stream from the steel. If the solution became too warm, a vigorous reaction set in at the surface of the iron, with a large increase of current. When about 0·50 gramme of the sample had dissolved, the rod was removed, scraped in a little nitric acid (2 cubic centimetres) contained in a watch-glass, washed at once, dried, and weighed. The liquid in the cell (and washings) was put into a test tube; a weight of the steel equal to that which had been dissolved was cut from the rod and dissolved in the same quantity of acid. The two tests were boiled for ten minutes and compared in the usual way. In all cases a large reduction in the amount of colour was found to be given by the sample dissolved in the cell and the tint was much greener; the same result was obtained with a quenched steel. Some of the results are given in the following table :

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[1] J. W. Cobb, *Journal of the Iron and Steel Institute*, 1911, No. I. p. 170.

TABLE XXV.—*Effect of Electrolytic Action on the Colour-Value.*

Sample.	Dissolved in Cell.	Dissolved as Usual.
	Cubic Centimetres.	Cubic Centimetres.
G—normal state	46·0	100·0
G—quenched state	42·0	100·0
Steel wire 0·90 per cent. carbon	50·0	100·0

To ensure that no experimental loss occurred in using the cell, blank tests were made in which the dry cells were omitted, the rod being allowed to dissolve in the acid in the ordinary way. It was found that the amount of carbon lost in transferring the solution to the test tube and cleaning the rod was very slight.

In all the above tests the precipitate obtained was almost black and dissolved rapidly in hot nitric acid. By varying the voltage other effects are possible; in one instance, with a low voltage, a precipitate was obtained which dissolved with great difficulty on boiling. The loss in colour does not occur if the action at the iron becomes too vigorous.

These experiments make it clear that the colour-value given by a steel sample is partly dependent upon the electro-chemical conditions which obtain while the metal dissolves. Any change in the structure which could cause an alteration in the electro-chemical action might therefore be expected to alter the colour-value given by the steel. In this connection the effect of strain produced by cold-work (and by quenching) must not be overlooked. Drillings are, of course, heavily cold-worked, and it was repeatedly found that they give higher colour-values than cut pieces of the same steels. In making these tests a piece weighing about 0·50 gramme was cut from the steel sample and an equal weight of drillings was taken from the same area so as to reduce to a minimum the possibility of error from any uneven distribution of the carbon. The two tests in each case were dissolved in equal quantities of acid at the same time and the temperature of the solutions was kept below 40° C. The cut pieces usually dissolved very slowly (one to two hours), and, therefore, if the differences found had been due to any great variation in the rates of decay of the brown precipitate, the drillings should have given the lower results. As a matter of fact it was found that such dissolved samples could stand for one day at 18° C., before boiling, without any appreciable change in the colour-value. Table XXVI. gives results which were obtained in the above way.

TABLE XXVI.—*Variations in Colour-Values given by Drillings and Cut Pieces.*

Sample.	Condition of Sample.	Drillings. Carbon Colour-Value.	Piece. Carbon Colour-Value.
		Per Cent.	Per Cent.
E	Annealed	0·42	0·35
G	Normal	0·42	0·33
J	Annealed at 680° C. 12 hours	0·60	0·58
Combined carbon 0·59 per cent. (Table XXIX.)	Normal	0·59	0·49
,, ,, ,,	Tempered 3 hrs. at 600° C. (Table XXXII.)	0·67	0·65
M	Normal	0·67	0·49
N	,,	0·78	0·69
Combined carbon 1·02 per cent. (Table XXIX.)	,,	1·02	0·80
G	Quenched	0·29	0·29

In each instance duplicate tests were made and the results agreed very well. The precipitates given by the drillings were always darker in colour and of a different character from those given by the cut pieces. The precipitates from the latter were much browner and, on boiling, dissolved in about one-half the time required to produce a clear solution of the drillings. Similar effects were obtained by well hammering pieces of annealed wire high in carbon; the colour-value of the hammered piece was increased 10 per cent. That this variation was not due to any difference in the rates of solution of the samples was shown by the fact that ten cut pieces dissolved much quicker than a single piece of the same weight, and yet the colour-values obtained were identical.

No explanation of the erratic nature of the results in Table XXVI. has been found, but there appears to be no alternative to the conclusion that the higher values given by the drillings are the résult of altered conditions produced through cold-work, most probably as it affects the electro-chemical actions in dissolving. The problems are very complex and a further investigation in this direction is in progress. The evidence already given, however, all tends to indicate that, although quenched and annealed samples yield such different results by the Eggertz test, these results may nevertheless be due to the presence of the same carbide in both cases, the variations in the amount of colour given by the colloid substances formed from the cementite being due on the one hand to the influence of the size and shape ot the carbide particles, and on the other to the extent and intensity of the electro-chemical action on dissolving.

PART IV.

THE CORRELATION OF THE BRINELL TEST AND THE COLOUR-CARBONS.

The observation was first made by Parker[1] that the results given by the Eggertz test can vary according to the heat treatment of the steel ; in this respect the method notably differs from other colorimetric methods used in steel analysis. A further investigation by Hogg[2] clearly showed that the widest differences are obtained in the results from quenched and annealed samples. In a similar way the physical properties of steel also vary with the heat treatment, and the question arises as to how far the variable results of the Eggertz test can be made use of to indicate the physical properties of the metal. For example, the same value for one physical property can often be obtained in two ways, either by cooling slowly through the critical range, or by cooling rapidly and afterwards tempering ; if the Eggertz result alone, when compared with the true carbon content of the steel, is to be a reliable guide to that value, the colour-carbon results should not differ in the two cases.

Many detailed investigations have been made upon the relations between the physical properties and the heat treatment of steel. To compare these in turn with the Eggertz test results would involve a very lengthy series of experiments; it seemed advisable, therefore, to select one more or less representative physical test so that, on correlating the results of this and the Eggertz test, when made on series of samples having different heat treatments, the information obtained would indicate whether further work on the same lines would be of any real value. The Brinell ball test for hardness offered several advantages and was therefore chosen. The test can be quickly made on relatively small pieces essential for perfect quenching, and the hardness value is, in a special degree, dependent upon the state of the carbon; also the effect of the grain size is not seen in this test as it is in some of the other physical tests.

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[1] *Loc. cit.*

[2] *Loc. cit.*

I. The Sulphuric Acid Method.

The recommendation of Eggertz, to match colours that are not quite the same to equal depths of tint, is one which certainly leads to discrepancies, as different observers have not always the same ideas in this respect, and one will dilute more than another a green tint when matching it with a browner tint. In order to eliminate this personal element as much as possible, a modification of the Eggertz test was sought in which these variations in colour were avoided. After a number of trials had been made, it was found that the addition of excess of sulphuric acid to the test solution brings the colours given by different steels much closer together, and although it was not found possible to obtain a perfect match in all cases, the colours given by the method are so nearly alike that variations in the results from the above cause are practically eliminated. The procedure is as follows: a suitable standard steel is chosen, containing about 0·90 per cent. of carbon when steels of widely differing carbon content are to be tested. 0·5 gramme of the sample is taken and a sufficient amount of the standard to give approximately the same colour-value as the sample is weighed out and made to 0·5 gramme with pure iron; if the colour-value of the standard is lower than that of the sample, then the latter must be divided instead, as it is essential that the colouring matters present in the two solutions should be about equal.[1] The tests are dissolved in the cold in 10 cubic centimetres of nitric acid (1·2), boiled for fifteen minutes, and cooled; 15 cubic centimetres of sulphuric acid (1–3 aq. by vol.) are then added to each and the solutions are colour-tested as described on p. 31.

The presence of sulphuric acid in the solution causes the iron salts to give a green coloration. The colour deepens with increasing additions of the acid, and reaches a nearly constant value when 15 cubic centimetres has been added; this amount need not, therefore, be measured with special accuracy. Unlike that of the carbon compounds, the iron colour does not decay on boiling and has, of course, the same value in all tests, since the small variations of the iron percentage in different steels can be neglected. Thus, it is evident that the ratio of the iron colour to the carbon colour in a test increases as the boiling is prolonged, and, in order to determine the colour-value of the carbon, it is necessary to know this ratio for the standard when boiled for the chosen period. In the ordinary Eggertz test, as given on p. 31, the standard is diluted so that the carbon colouring matter is contained in a volume in cubic centimetres equal to two hundred times the percentage of carbon. When sulphuric acid is used this volume is increased by a number of cubic centimetres sufficient to dilute the coloured iron salts to the same intensity as the carbon colour; this iron-value is then deducted from the volume of the matched sample before the carbon percentage is calculated by simple proportion. As the result of a number of experiments the value to be allowed for the iron salts at different periods of boiling was found to be as follows:

TABLE XXVII.—*Iron-Values in the Sulphuric Acid Method.* (0·5 *gramme sample. Dilution* 200 × *per cent. Carbon in Cubic Centimetres.*)

Period of Boiling.	Iron-Value.
10 minutes	47 cubic centimetres
15 ,,	52 ,,
20 ,,	56 ,,
25 ,,	60 ,,

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[1] Of course, if the samples to be tested have about the same colour-values a similar standard steel can be selected and need not be divided. Division is only necessary when the same standard must be used for a wide range of steels.

Thus, in working the method, a standard containing 0·80 per cent. of carbon, boiled for fifteen minutes, is diluted to (200 × 0·8 + 52) = 212 cubic centimetres, and 52 cubic centimetres is deducted from the volume of the sample before dividing to obtain the colour-carbon. It can be shown that an error of 5 cubic centimetres in this value makes very little difference, provided that the colour intensities of standard and sample are similar.[1]

Apart from diminishing any error due to a wrong iron-value, the necessity of having approximately the same amounts of colouring matter in standard and sample solutions arises from the fact that the iron tint and the carbon tint are not quite alike, the former being the greener. As the colours given by different steels can be made to match much more closely by this method, there is no doubt that the sulphuric acid alters the tints of the colouring matters. It was found that the addition of sulphuric acid to solutions of the colouring compounds A and B (p. 41) in nitric acid caused no change whatever in the tints in the absence of iron, and it is therefore evident that the sulphuric acid must act by altering the form in which the iron is attached to these substances (p. 44). Most probably the nitrate and hydrate are largely changed to ferric sulphate. The change is instantaneous, and it was found, by adding nitric acid after the sulphuric acid, that all "excess colour" had been removed by the latter. The brown compound A will be only very slightly altered in colour as it does not react with the iron to any great extent. Solutions of annealed steels,

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[1] Let I = true iron-value in cubic centimetres,
$I + \alpha$ = actual iron-value taken (α = error),
S = carbon ("points") in the standard steel.
S_1 = carbon ("points") in the sample.
Then the correct volume for the standard = $2S + I$.
the actual volume of the standard test = $2S + I + \alpha$.
the correct volume for the sample = $2S_1 + I$.

The actual volume of the sample test when matched $= \dfrac{(2S + I + \alpha)(2S_1 + I)}{2S + I}$

and the carbon-value obtained

$$= \frac{1}{2}\left[\frac{(2S + I + \alpha)(2S_1 + I)}{2S + I} - (I + \alpha)\right]$$

$$= \frac{2SS_1 + S_1 I + \alpha S_1 - \alpha S}{2S + I}$$

$$= S_1 + \frac{\alpha(S_1 - S)}{2S + I}$$

Example:—Let $S = 40$, $S_1 = 60$. $I = 50$, $\alpha = 5$,

then the resulting error $= \dfrac{\alpha(S_1 - S)}{2S + 1} = 0{\cdot}75$ point.

It is clear that as the values for S and S_1 approach each other, the error becomes smaller and entirely vanishes when the values are the same. Thus it is advisable to arrange the test so that the amounts of colouring matter in standard and sample are approximately equal.

which contain a relatively larger amount of this substance than those of air-cooled and quenched samples, are, therefore, a little browner in tint, but owing to the presence of the iron colour the effect of the brown substance is minimised and the differences in the tints given by such samples are much less than in the ordinary method.

The sulphuric acid method, though somewhat complicated in description, is quite easy to work, and yields consistent results in cases where the variation in tints renders the ordinary Eggertz test uncertain. In Table XXVIII. a comparison is made between the results given by the ordinary Eggertz test and the sulphuric acid method on the series of steels from which photos 1–6 were taken (p. 71). It will be seen that as the carbide becomes finer and the tint greener the ratio of the colour-value to the carbon content decreases more rapidly by the sulphuric acid method, this change having been largely compensated by the manner in which the same "depths of tint" were obtained in the ordinary method. Of course, the latter method is distinctly preferable in cases where the carbon content is required, but not so when the "missing" carbon is to be measured.

TABLE XXVIII.

Sample.	Carbon in Sample.	Eggertz Test Result.	Sulphuric Acid Test Result.	Increase in Colour in H_2SO_4 Test.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
E	0·37	0·42	0·45	21·5
R	1·39	1·41	1·59	14·5
C	0·28	0·285	0·31	11·0
G	0·42	0·42	0·45	7·0
N	0·78	Standard	Standard	...

It has recently been shown by Le Chatelier and Bogitch[1] that the percentage of manganese in standard and sample should be similar in order to obtain the most satisfactory results by the Eggertz method. The effect of an increasing manganese content is to retard the growth of the carbide particles, and, as a general rule, the colour-values of samples, having a similar heat treatment, decrease as the manganese content is raised. It is possible that the isomorphous manganese carbide in the cementite of ordinary steels may give rise to less colour than pure iron carbide as suggested by Arnold and Read,[1] but, in view of the results given in Table XXVIII., it seems most likely that the effect of manganese in reducing the colour-value can be completely explained by its action in retarding the growth of the cementite. In any case, after due allowance has been made for this, the reduction in colour-value directly due to isomorphous manganese carbide cannot be large.

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[1] *Comptes Rendus*, 1916, vol. 162, pp. 709, 731.

II. Comparison of the Eggertz Results with the Brinell Hardness given by a Series of Quenched Steels.

In order to ascertain if any relationship existed between the Brinell hardness and the total "missing" carbon of quenched steels, a series of samples was selected, chiefly from those described in Table I., in which the carbon content varied between 0·21 per cent. and 1·39 per cent. Three additional samples were used (Nos. 1, 5, and 9, Table XXIX.). No. 1 was taken from an acid steel plate, No. 5 was cut from a 4-inch square basic steel billet, and No. 9 from a bar of chisel steel. These samples were of uniform composition and practically free from segregation. A piece about 1 inch square and ⅜ inch thick was cut from each and placed in a muffle furnace which had been brought to the temperature required to give an even distribution of the carbon in solid solution, as indicated in Table XXIX. After standing at that temperature for several minutes, the specimen was rapidly quenched in water at about 10° C. The sections were next ground on the wet grindstone to remove the partially decarburised surfaces, and the Brinell hardness number of each was then obtained. It was found that this value remained practically constant between 0·50 and 1·00 per cent. of carbon, as has been shown by McCance.[2] The colour-value of the quenched section of sample N (combined carbon, 0·78 per cent.), when compared with the same sample in the normal condition, was first ascertained by the sulphuric acid method; several concordant estimations showed it to be 0·43 per cent. This section was then taken as standard, and from it the colour-values of the other quenched pieces were determined by the ordinary Eggertz method (p. 31). The results are given in Table XXIX., together with the Brinell hardness numbers. It will be seen that the greatest proportion of colourless products is given by samples containing about 0·90 per cent. of carbon, a result which is in complete agreement with that obtained by Hogg.[1]

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[1] *Journal of the Chemical Society*, 1894, Trans., p. 788.

[2] *Journal of the Iron and Steel Institute*, 1914, No. I. p. 192.

TABLE XXIX.—*Eggertz Results and Brinell Hardness of Quenched Steels.*

No.	Sample.	Carbon per Cent.	Manganese per Cent.	Quenching Temperature.	Colour-Value.	"Missing" Carbon.	Percentage of Total Carbon as "Missing."	Brinell No.
1	...	0·21	0·70	920° C.	0·16	0·05	24	250
2	C	0·28	0·44	900° C.	0·19	0·09	32	480
3	G	0·42	0·64	860° C.	0·29	0·13	31	550
4	J	0·54	0·95	810° C.	0·34	0·20	37	630
5	...	0·59	0·77	800° C.	0·36	0·23	39	600
6	M	0·71	1·30	,,	0·395	0·315	44	620
7	N	0·78	0·75	,,	0·43	0·35	45	600
8	P	0·84	0·79	,,	0·46	0·38	45	660
9	...	1·02	0·40	810° C.	0·67	0·35	34	650
10	R	1·39	0·40	950° C.	0·99	0·40	29	510

The curve, Fig. 17, shows the relation between the total carbon content and the Brinell hardness of the quenched pieces; the curve, Fig. 18, indicates the relation between the colour-carbon and the total carbon of the samples. These results make it quite clear that the hardness of quenched steels as indicated by the Brinell ball test is not dependent upon the total amount of "missing" carbon; for example, sample 10 contains twice as much as sample 4, and yet its hardness number is less.

The deficiency in the proportion of "missing" carbon in the samples containing less than 0·70 per cent. or more than 0·90 per cent. of carbon appears in spite of the most careful quenching. Samples 1, 2, 3, 9, and 10, on dissolving in the cold, yielded appreciable quantities of a flocculent gelatinous precipitate which did not readily dissolve on boiling, and differed in this respect from the traces of precipitate given by the intermediate quenched samples (Nos. 4–8). On examination under the microscope these gelatinous precipitates were found to have a structure very similar to that of the precipitates obtained by dissolving a fully quenched sample in very weak acid (p. 38, photo. 20), or a slightly tempered steel in the usual acid (1·2) (see p. 91). The tints given by these

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[1] *Journal of the Iron and Steel Institute*, 1896, No. II. p. 179.

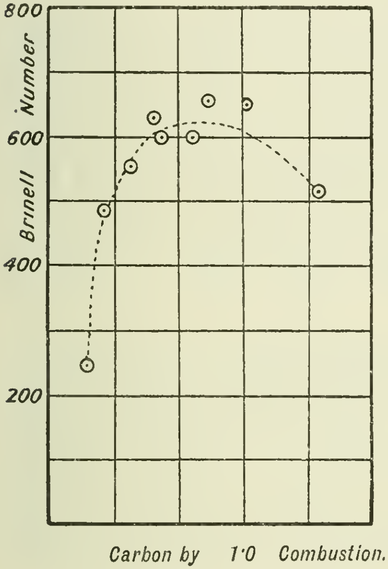

Fig. 17.—Hardness of Quenched Steels.

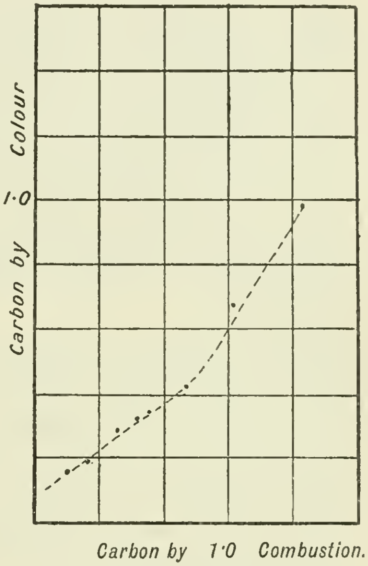

Fig. 18.—Eggertz Test on Quenched Steels.

samples were distinctly redder than those of the intermediate steels. These facts certainly suggest that the deficiency in "missing" carbon arises from the incomplete preservation of the solid solution which leads to the precipitation of part of the carbide, so that some of the particles of the brown substance, formed from the coarser carbide particles, are sufficiently large to resist the solvent action of the acid and coalesce into the gelatinous masses which dissolve with difficulty; exactly the same result is observed with quenched steels after tempering at about 250° C. for two hours.

With the higher carbon (austenitic) samples a certain amount of this brown gelatinous precipitate is formed even after quenching in iced brine. This may well be due to the fact that, in such samples, the solid solution is unstable throughout a cooling range which increases rapidly as the carbon rises above 0·9 per cent. ; thus, for 1·4 per cent. of carbon, the separation of cementite will be possible throughout the whole range below 920° C., whereas, with 0·9 per cent. of carbon, it is only possible below 690° C. In the case of the low carbon steels, the insufficiency of the quenching may be due partly to the difficulty, in the absence of much carbon, of retaining the gamma iron (which alone dissolves the carbon). Thus, on quenching sample 1 (Table XXIX.) from 710° C. after it had been heated to 760° C., the colour-value was thereby reduced to 0·14 per cent. This heat treatment causes the carbon to concentrate in areas which approximate the eutectoid composition, in which the carbide does not so readily begin to coalesce in the cooling, and as a consequence more "missing" carbon was obtained.

Quenching from Different Temperatures.—A series of experiments was next made by quenching sections of the same steel from different temperatures. The method employed was the same as that already described, and the quenching temperatures were 720°,[1] 800°, 900°, and 980–1000° C. After the Brinell hardness had been measured, the sections were crushed and their colour-values compared by taking one as standard. The results of experiments made in this way on three different steels are given in the following table:

TABLE XXX.—*Effect of Quenching from Different Temperatures.*

Quenching Temperature.	Sample J (combined carbon, 0·54 per cent.).		Sample N [2] (combined carbon, 0·78 per cent.)	Sample P (combined carbon, 0·84 per cent.).	
	Brinell No.	Colour-Value.	Colour-Value.	Brinell No.	Colour-Value.
Degrees C.		Per Cent.	Per Cent.		Per Cent.
720	600	0·34	0·43	630	0·46
800	630	0·345	0·43	650	0·46
900	630	0·34	0·425	630	0·445
980–1000	600	0·33	0·425	630	0·445
1150	...	...	0·425	...	...

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[1] The section was first heated to 760° C. and then lowered quickly to 720° C.

[2] Brinell hardness not taken.

The slight differences in the colour-values of each series are well within the limits of experimental error, and no evidence was found of any real variation in the colour-values of such steels when quenched from the above temperatures.

III. Comparison of the Eggertz Results with the Brinell Hardness given by Series of Tempered Steels.

A number of similar sections about $\frac{3}{8}$ inch thick were cut from sample J and thoroughly quenched in cold water from 800° C. The Brinell hardness of each was measured and was found to be the same (630) throughout. The pieces were then reheated for two hours as follows: the first (together with a crushed portion of it for the colour-test) at 100° C. in boiling water; the second, third, fourth, and fifth (with crushed portions) were wrapped in iron gauze and heated under mercury at 150°, 200°, 250°, and 300° C. respectively. The remaining sections were heated in nitrogen at temperatures varying between 350° and 660° C.; these sections were drilled for colour-testing.

The Brinell hardness number of each was again determined after tempering. In ascertaining the colour-values of these tempered sections, the sulphuric acid method was used, and sample N in the normal state was taken as standard. As a check, the colour-values were also found, in certain cases, by the ordinary Eggertz method. The hardness numbers and colour-values obtained are shown in the following table:

TABLE XXXI.—*Results given by the* 0·54 *Carbon Steel J when Tempered* (*two hours*).

Temperature of Reheating.	Hardness No.	Sulphuric Test Results.	Eggertz Test Results.	"Missing" Carbon.
Degrees C.		Per Cent.	Per Cent.	Per Cent.
...	630	0·345	...	−0·195
100	630	0·365	...	0·175
150	550	0·40	0·41	0·14
200	510	0·40	0·41	0·14
250	480	0·51	0·52	0·03
300	440	0·53	0·54	0·01
350	430	0·535	...	0·005
400	375	0·58	0·57	+0·04
460	340	0·60	...	0·06
530	300	0·61	...	0·07
600	210	0·62	...	0·08
650	195	0·645	...	0·105
660	195	0·67	...	0·13

These results have been plotted in Fig. 19 ; curve A shows the decrease in hardness with increasing temperature of reheating and curve B the change in the values for the "missing" carbon. It will be observed that on tempering at 400° C. the colour-carbon found, when using the sample N as standard, is higher than the actual amount of carbon present. The "missing" carbon has here become a positive quantity.

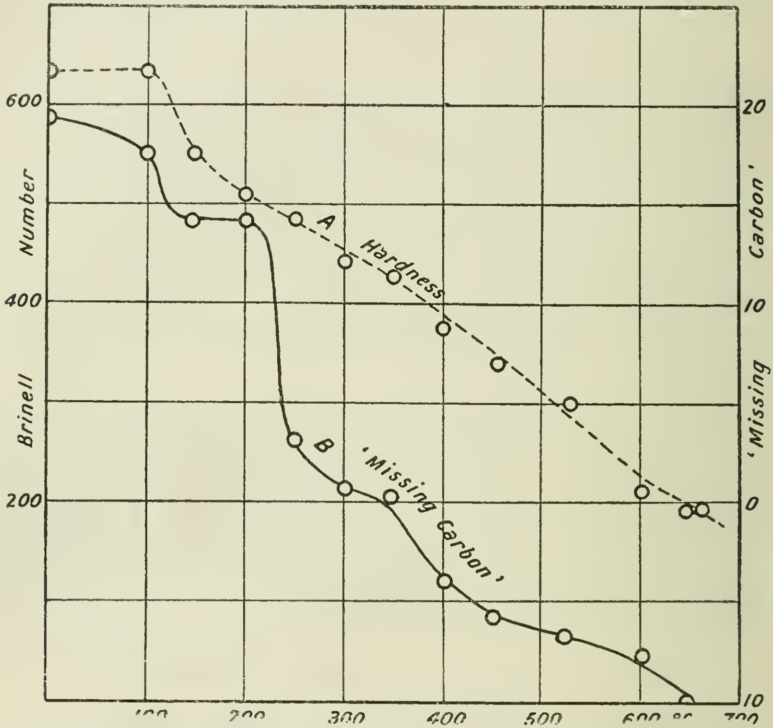

Fig. 19.—Relation between Brinell Hardness, Eggertz Test, and Temperature of Tempering. Sample 0·54 Carbon Steel (see Table XXXI.), Tempered 2 Hours.

A second series of similar tests was next made on sections of the billet containing 0·59 per cent. of carbon (see Table XXIX., No. 5). In this series the time of heating was increased to three hours, and at temperatures from 250° C. upwards the sections were heated in nitrogen and afterwards drilled. The colour-values were obtained in the same way as in the previous series, and are given in Table XXXII. together with the hardness numbers. These results are also plotted in curves A and B, Fig. 20 (p. 92), and it will be seen that they are very closely similar to those given by the first series.

TABLE XXXII.—*Results given by* 0·59 *Carbon Steel when Tempered* (*three hours*).

Temperature of Reheating.	Hardness No.	Sulphuric Acid Test Results.	Eggertz Test Results.	"Missing" Carbon.
Degrees C.		Per Cent.	Per Cent.	Per Cent.
...	600	0·36	...	−0·23
100	600	0·395	...	0·195
145	555	0·43	0·44	0·16
200	515	0·43	0·44	0·16
255	495	0·54	0·54	0·05
300	475	0·55	0·545	0·04
350	430	0·57	0·59	0·02
400	390	0·61	0·60	+0·02
450	375	0·62	0·63	0·03
500	320	0·65	...	0·06
600	240	0·69	...	0·10

In both series the crushed portions of the specimens which were heated below 250° C. gave, on dissolving in nitric acid (1·2), a coloured solution similar to that given by the quenched sample. The colour-values gradually rose, and the small amount of brown precipitate was slightly increased with the increasing temperature; this caused the diluted tests to appear a shade redder. On dissolving the samples which had been reheated at 250° C., a very marked change was observed. In both instances the solutions contained a large quantity of brown precipitate. This, when examined under the microscope, was found to consist of gelatinous masses having an exceedingly fine granular structure, but otherwise very similar to those shown in photo. 20, which were obtained by dissolving a quenched steel in weak acid at room temperature. This similarity of the two was also seen in the slow rate at which they dissolved in nitric acid (1·2). In the first series, fully half an hour was required to effect a complete solution by boiling, as in the case of the precipitate from the quenched steel; in the second series, about twenty minutes was necessary. "Delay" in dissolving must cause an increase in the colour-value as in the case of annealed steels (p. 70), and the sudden rise in colour-value at 250° C. is probably largely due to this effect, especially as the previous test (200° C.) contained a relatively small amount of precipitate. It has been shown (p. 69) that, on dissolving at 100° C. steel containing coarse carbide particles, a hardening action occurs which still further increases the " delay " ; no such action takes place on treating, in the same way, the samples tempered at 250° C. ; the rate of solution of the precipitate is unaltered and the colour-value is not increased. Further work indicated that the precipitates which first appear in any bulk after tempering for two hours are not so difficult to dissolve as those obtained when a slightly higher temperature has been used ; this effect seems to attain a maximum with tempering temperatures between

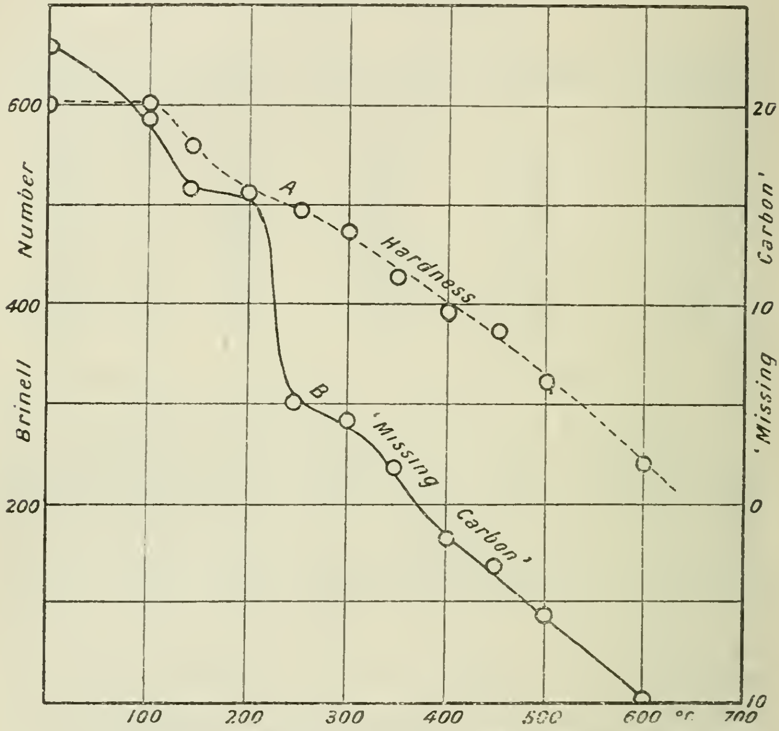

Fig. 20.—Relation between Brinell Hardness, Eggertz Test, and Temperature of Tempering. 0·59 Carbon Steel, Tempered 3 Hours.

250° C. and 300° C. The rate of solution of the precipitate from samples tempered at 400° C. is normal.

It was found (by dissolving in the cold, filtering, and comparing the filtrates) that the amount of precipitate given by the above samples (250° to 300° C.), and also by the quenched steels, 1, 2, 3, 9, and 10 of Table XXIX., decreased as the acid strength used was increased from 1·10 to 1·30 sp. gr. The most satisfactory explanation of these results appears to be that the formation of a precipitate depends upon the size of the carbide and upon the strength of the acid employed. Thus, in the case of the steels tempered at 250° C., the average size of the carbide particles has become sufficiently large to enable the particles of the brown substance to resist the solvent action of the acid and to agglomerate into large masses, just as does the brown substance formed on dissolving quenched steels in weak acid. If the average dimension of the carbide particles in these tempered steels could be ascertained, the smallest size of particle capable of forming brown precipitate in the Eggertz test would be known.

At first sight, the sharp drop in the "missing" carbon which occurs between 250° and 300° C. might be regarded as due to a sudden change in the state of the carbon, while the formation of a bulky precipitate at 250° C. would indicate the temperature at which cementite was precipitated from the solid solution. The entire absence of any corresponding feature in the hardness curve seems an almost conclusive proof that such is not the case; the discontinuity in the colour-values must be explained rather by the peculiar reactions of the colloidal substances, as described above, than by any important change in the state of the carbon.

The growth of the cementite in tempered steels takes place under different conditions from those which accompany the formation of pearlite in slow cooling through the critical range. Pearlitic structures have their origin in the crystallisation of free cementite and ferrite in contact with a stable solid solution of carbide (or carbon) in iron, and this solution acts as a medium for the rapid diffusion of the carbon. In accordance with the principles governing crystal-growth, the crystal-nuclei of cementite as they are formed will be more soluble than the coarser particles already present, and this will cause the larger particles to grow at the expense of the smaller; hence, the slower the cooling through the critical range the coarser will be the resulting pearlite, up to the point at which the eutectoid structure begins to be destroyed by "divorcing." In tempering steels no such stable solid solution is present to afford a medium for the rapid diffusion of the carbon, since carbide is at most only slightly soluble in alpha iron. Thus, the carbide growth must be compared, in this instance, rather to the coalescence of suspended drops in a liquid than to the growth of a crystal in contact with its solution.[1] This analogy has been discussed in some detail by Benedicks.[2] The two cases, however, are not exactly comparable, since liquids possess no orientated structure, whereas iron is a crystalline substance. The fineness of the carbide in the early stages of tempering undoubtedly gives it considerable mobility, and in the crystalline medium the coalescence of the carbide may well take place most easily along certain crystal planes and interfaces.

The evidence obtained from the examination of the precipitates given by the pieces tempered between 250° C. and 450° C. supports this view, as at about 350° C. the finely granular gelatinous masses begin to be replaced by agglomerations of extremely fine sheets of the substance, similar, in many respects, to those given by fine pearlite (p. 35). Sections of such tempered specimens, when examined, show a structure somewhat resembling martensite, especially with the lower carbon steels, and it thus seems very probable that the needle-like outlines are caused by thin layers of carbide deposited along the crystal-planes or interfaces. The maximum solubility in sulphuric acid which occurs at about 400° C., as shown by Heyn and Bauer,[3] would thus be due to the presence of the greatest number of such carbide layers whereby the electrolytic action in dissolving would be at a maximum. As the very fine sheets of the substance seen in the brown precipitate have, no doubt, swelled greatly, it is not surprising that the carbide layers from which they were formed cannot be detected with certainty under the microscope. With a further rise in the tempering temperature the carbide begins to be visible, and dark granulations, or nuclei, appear in the sheets of the precipitates, as shown in photo. 15. This effect very strongly suggests that the carbide layers are breaking up into separate granules which are then large enough to be detected. The dark rods of the substance as seen in the photograph also appear at this stage, especially with steels not containing manganese. With increasing temperature the granules of cementite gradually become larger and are quite visible in sections of steel tempered at 500° C. for two hours. The precipitate again changes at this stage, and the compact, unswollen form of particle appears ; as the temperature of tempering is raised above this point, the size of the brown particles increases with the increasing size of carbide, but no further change in the character of the precipitate takes place. This last form of precipitate can be hardened by dissolving at 100° C. (p. 69), and in every other way behaves similarly to that given by the very coarse carbide of drastically annealed steels. The size of the carbide, as seen in sample J after tempering at 660° C. (Table XXXI.), is shown in photo. 19.

---

[1] In the present Report the term "pearlite" has been used in its original sense, to describe the true eutectoid structure formed on cooling through the critical range. A separate name seems desirable to distinguish the uniform granular carbide structure found in tempered steels (photo. 19), which, of course, is not eutectoid.

[2] *Journal of the Iron and Steel Institute*, 1908, No. II. p. 153.

[3] *Ibid.*, 1909, No. I. p. 109.

In the absence of manganese or any such element in the steel, the changes which occur on tempering appear to take place as just described for temperatures below 400° C., but with higher temperatures, in several instances, practically the whole of the carbide was found to migrate to the crystal boundaries. The precipitate obtained from a section of sample H, which had been quenched from 850° C. and then heated for two hours at 400° C., is shown in photo. 15, and the structure of the steel, obtained by etching slightly with picric acid and afterwards with sodium picrate, is shown in photo. 12. The precipitate consisted of masses of exceedingly fine sheets which contained rows of dark granulations and, as already explained, the character of these precipitates indicates that the carbide lies chiefly in the planes. That there is a tendency for the carbide to move to the boundaries of the grains, however, can be seen in photo. 12, and after tempering at 550° C. the greater portion of the carbide was found to have so migrated as shown in photo. 13 ; the type of precipitate given by this section is seen in photo. 16. After tempering a third section at 660° C., practically all the visible carbide had moved to the crystal margins and photos 14 and 17 show the carbide and precipitate of this section.

The colour-values and hardness numbers for these three pieces are given in the following table :

TABLE XXXIII.—*Results given by Sample H (combined carbon,* 0·50 *per cent.) when Tempered (two hours).*

Temperature of Reheating.	Hardness No.	Eggertz Test Results.
Degrees C.		Per Cent.
400	248	0·50
550	178	0·58
660	151	0·62

It will be seen from the curves in Figs. 19 and 20 that, although the relation between the "missing" carbon and the hardness is not proportional throughout, an approximate idea of the hardness can be obtained from the Eggertz results. In order to compare these values with those given by the same steel when cooled more or less quickly through the critical range, three sections of sample J were taken, and after heating to 800° C. the first was cooled in water at about 80° C., the second was cooled a little more slowly, and the third was allowed to cool in the furnace. The colour-values and hardness numbers of these were obtained and are given in Table XXXIV., together with the colour-values of the tempered sections which gave the nearest hardness number (Table XXXI.).

TABLE XXXIV.

	Sections Cooled from 800° C.			Tempered Sections.		
	Hardness No.	Eggertz Result.	Filtrate Colour-Value.	Hardness No	Eggertz Result.	Filtrate Colour-Value.
		Per Cent.	Cubic Centimetres.		Per Cent.	Cubic Centimetres.
1	430	0·49	63·0	430	0·535	27·0
2	248	0·53	45·0	300	0·61	23·0
3	195	0·54	36·0	195	0·67	18·0

In the same way, results similar in character were obtained from the steel used in the second series of tempering tests (Table XXXII.). These experiments make it quite clear that the Eggertz result cannot be used to indicate, with any degree of certainty, the hardness of a steel unless the previous heat treatment of the sample is known.

The pearlitic structure of the furnace-cooled sample No. 3 is shown in photo. 18, and the carbide of the tempered section with the same hardness is seen in photo. 19. Both specimens were stained with sodium picrate, after first lightly etching with picric acid, and in the latter photograph only the size of the carbide is shown and not the amount, as some of the particles appeared to be removed during the staining process. It will be observed, on comparison of the above results with those in Table XXXI., that tempered sections giving the same colour-values as the specimens cooled from 800° C. are uniformly harder; at the same time, the size of the carbide in these specimens was seen to be very much smaller. For example, the pearlite of the slowly cooled sample No. 3 (photo. 18) was easily visible, whereas the carbide in the tempered sample No. 1, which had the same colour-value, could not be detected. Again, the carbide in the annealed steel E (photo. 6) is manifestly much larger than that of the tempered sample No. 3 (photo. 19), and yet the increase in colour-value given by the latter was relatively greater than that given by the former. These and similar comparisons clearly demonstrated the fact that, while with tempered steels also the increasing size of carbide is accompanied by an increasing colour-value, the carbide dimensions are on a much smaller scale than in the air-cooled and annealed steels that give the same colour-value.

"*Hardening*" *Carbon.*—The largest amounts of the so-called "hardening" carbon must occur in completely quenched steels, and such samples, on dissolving in the cold, yield coloured solutions almost free from precipitate. If, therefore, the greater hardness of any of the tempered sections referred to above is due to the presence of more "hardening" carbon, this should be indicated by a higher colour-value of the filtrate when compared with a similar filtrate given by the softer sample having the same colour-value after cooling from 800° C. In order to ascertain whether this was the case, 0·25 gramme portions of each of the six samples were tested by the method given by Campbell and Haskins[1] for estimating the "carbides soluble in the cold." This method is the same as that which was employed by Jüptner[1] in determining the "hardening" carbon in steel. The six tests were made together, and the colour-values of the filtrates were found by taking the lowest as standard. The results are given in Table XXXIV. under the heading, "Filtrate Colour-Values." It will be seen that the tempered sample No. 1 has nearly twice the hardness of the quickly cooled sample No. 2; if this were due to the presence of more "hardening" carbon the colour-value of the filtrate of the tempered section should have been higher than that of the quickly cooled sample. Exactly the opposite is the case, however, the colour-value of the filtrate from the harder steel being only three-fifths of that from the softer steel. Again, if the hardness were due to the presence of "carbides soluble in the cold," then similar steels of the same hardness should at least give approximately the same colour-values in the filtrates. This is not confirmed by the results in Table XXXIV., where it is evident that there is no direct relationship between the filtrate colour-values and the hardness of the samples.

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[1] *Loc. cit.*

The hypothesis, that the continuous increase in the colour-values of the tempered series is due to the gradual decrease in the quantity of "hardening" carbon, seems to require, at each temperature of tempering, a slow transition of this form of carbon to cementite. At the lower temperatures (say 150° C.), as the colour increase is only slight, this reaction must reach a limit. With a further rise in temperature this limit must extend so that a little more cementite is formed, and so on. This arrest in the reaction at the different temperatures is extremely difficult to explain on the simple view that one form of carbide is changing to another; such a transition, when once started, should proceed to a finish as a reaction in the opposite direction does not seem possible in this case. If, however, the view is accepted that the carbon in quenched steels already exists as cementite, it can readily be understood that the mobility and further growth of the cementite particles, at a given temperature, is greatly restricted when each particle has attained a given size. The rise in the colour-values shown in Tables XXXI. and XXXII. will thus be the effect of a continually increasing carbide size, which will be accompanied by variations in the electro-chemical action on dissolving due to the energy changes which are well known to occur.

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[1] *Loc. cit.*

In conclusion, the author wishes to express his indebtedness to Mr. A. F. Hallimond, M.A., for his assistance in the course of this investigation, especially in the working out of the sulphuric acid test and experiments on the decay-curves, and in the preparation of the manuscript.

SUMMARY.

Part I.

1. A method is described for the estimation of small amounts of carbon dioxide by absorption in ammoniacal barium chloride solution.

Part II.

2. By means of the above method, the carbon content of the gases evolved in the Eggertz test is ascertained. The principal gas, carbon dioxide, is given off, at a decreasing rate, during several hours' heating, in amounts closely proportional to the percentage of carbon in the steels, irrespective of heat treatment, except in the case of austenitic samples. A suggested new method, based on this reaction, is described.

3. Hydrocyanic acid is slowly evolved also, and originates during the solution of the sample ; its amount is independent of the heat treatment, and manganese or nitrogen content of the steel, but shows unaccountable variations.

4. Only a very minute quantity of hydrocarbon (and possibly carbon monoxide) is evolved when the test solution of either a normal or a quenched steel is heated.

5. A steel containing 1·0 per cent. of combined carbon will yield, in the first ten minutes' boiling, 22·0 per cent. of the carbon as carbon dioxide, 5·0 to 10·0 per cent. as hydrocyanic acid, and 2·0 to 3·0 per cent. as hydrocarbon gas.

6. Contrary to the results of Osmond and Werth, the "missing" carbon is not evolved as a hydrocarbon or other compound in the gases ; its presence in the solution is confirmed by oxidation with potassium permanganate.

Part III.

7. The colloidal nature of the colouring matter and the existence of two colouring compounds (or groups of compounds) are shown by the examination of the solution of the precipitate by dialysis. The two substances are termed A and B, the latter being formed from the former by the action of nitric acid ; both react with the iron in the solution, which causes a change of tint and, in the case of the substance B, a large increase in the amount of colour.

8. The rates of colour-decay on heating the test solutions and solutions of the colouring substances A and B are determined, and it is shown that the green body B is slowly changed to a colourless (or only slightly colouring) compound. The presence of colourless substances in the tests of both quenched and normal steels is also demonstrated, a greater proportion being present in quenched steel tests and as " missing " carbon these substances are shown to be formed on dissolving. In both cases the colourless products increase in relative amount on boiling.

9. Several reasons are given for regarding the green colouring matters present in the solutions of both normal and quenched steels as identical.

10. Variations in the colour-values of different steels, when compared with the true carbon content, are shown to be brought about in at least two ways, one by delay in the solution of the precipitate and the other by the early formation of excess of colourless products. These two effects may overlap and their separate amounts cannot often be ascertained.

11. The influence of the size of the carbide in the steel on the Eggertz test results has been studied. The particles of the brown precipitate are shown to resemble in shape the carbide particles from which they were formed ; as the carbide decreases in size the precipitate is more gelatinous and yields greener tints.

12. Reasons are given showing that the presence of a green tint in the solutions of ordinary steels does not necessarily indicate the presence of " hardening " carbon in the steel.

13. Experiments in which the steel was dissolved under varying conditions of electro-chemical attack showed that this

influences the colour-value; increased voltage in some cases lowers the colour, while cold-worked samples generally give higher results.

Part IV.

14. A modification of the Eggertz test is given in which sulphuric acid is used. Variations in tint are thereby greatly reduced.

15. The Eggertz results on quenched steels have been compared with the Brinell hardness numbers. No simple relation has been found.

16. The Eggertz results have been correlated with the Brinell hardness of samples quenched and tempered at various temperatures. These show that the colour results are by no means simply related with the hardness.

17. Comparison of the results given by the same steel when tempered and when air-cooled at varying rates shows that, for equal colour-values, the hardness is greater in the tempered steel while the size of the carbide is much less.

18. The colour-value of a steel is shown to be greatly influenced by the following:

A. The heat treatment and composition of the steel as they affect the size and shape of the carbide particles.

B. The electrolytic action in dissolving (Part III.). As drillings usually give higher results than cut pieces, it is very probable that cold-work affects the result by changing the electrochemical action.

19. Although the form in which the carbon exists in quenched steels has not been definitely ascertained, the evidence advanced throughout the paper strongly indicates that it is still present as cementite.

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THE CHEMICAL DETECTION OF STRAIN IN IRON AND STEEL BY THEIR REACTION WITH NITRIC ACID.[1]

By J. H. WHITELEY and A. F. HALLIMOND, M.A.
(South Durham Steel and Iron Co., Ltd., Stockton-on-Tees.)

INTRODUCTION.

The research here recorded is the outcome of an observation made in the course of experiments in connection with the Eggertz test for combined carbon which have recently been described by one of the authors.[2] In examining the composition of the gases given off when samples of steel are dissolved in dilute nitric acid, it was noticed that the nitrous gases were evolved in differing proportions by different samples. At first these variations were thought to be due to the influence of the other elements, such as carbon and phosphorus, present in the steels, but subsequent work showed that the main cause of the variations was to be found in the mechanical treatment to which the samples had been subjected.

Before describing the work done in the application of this effect to the detection of strain, it will be necessary to discuss in some detail the chemical reactions which take place when iron is dissolved in nitric acid. This forms the subject of Part I. of the present Report. In Part II. the changes in the reaction brought about by deformation of various iron and steel samples are described, and it is shown how the effect can be used to measure the progressive removal of cold-work on annealing.

PART I.

The Analysis of the Gases formed on Solution of Iron in Nitric Acid: the Chemical Reactions Involved.

The reaction of nitric acid with various metals has been the subject of many investigations. Among these numerous researches

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[1] Received March 6, 1918.

[2] J. H. Whiteley, *Carnegie Scholarship Memoirs*, vol. viii., 1917.

may be mentioned those of Divers,[1] Montemartini,[2] and Stansbie,[3] while several of the earlier papers have been discussed by Veley [4] in his own work on the subject. Attention has, however, been chiefly directed to the reactions of metals such as copper, while iron and similar elements have not received so much careful study.

A variety of reduction products is obtained when the metals are dissolved in nitric acid; nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, ammonia, hydroxylamine, and hydrogen have all been found in proportions which vary with the metal used, and with the temperature and concentration of the acid. The complete analysis of such a mixture is both tedious and difficult; fortunately, in the case of iron, several of the products most difficult to estimate are either not formed or are present in amounts so small as to be negligible in the present investigation. Hydroxylamine and hydrazine have not been detected, and although numerous tests were made for hydrogen it was never found to be present in the evolved gases. The chief products to be estimated are therefore nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, and ammonia. No completely satisfactory explanation of the mechanism of the reactions by which these products are formed has yet been obtained, but whatever theory of the intermediate stages be adopted, the quantities of iron and nitric acid required to yield these final products of the reduction are given by the following equations, in which it is assumed that the iron in all cases is entirely transformed to ferric nitrate, a condition which is probably always fulfilled when the solutions have been boiled.

$$\begin{array}{ll}
(1) & \mathrm{Fe + 6HNO_3 = Fe(NO_3)_3 + 3NO_2 + 3H_2O.} \\
(2) & \mathrm{Fe + 4HNO_3 = Fe(NO_3)_3 + NO + 2H_2O.} \\
(3) & \mathrm{8Fe + 30HNO_3 = 8Fe(NO_3)_3 + 3N_2O + 15H_2O.} \\
(4) & \mathrm{10Fe + 36HNO_3 = 10Fe(NO_3)_3 + 3N_2 + 18H_2O.} \\
(5) & \mathrm{8Fe + 27HNO_3 = 8Fe(NO_3)_3 + 3NH_3 + 9H_2O.}
\end{array}$$

According to these equations the approximate volume of each gas at N.T.P. which can be formed by one gramme of iron is that given in the second column below, while the weight of iron which will produce one cubic centimetre of gas is that in the third column.

---

[1] *Journal of the Society of Chemical Industry*, 1904, 23 (24), 1182–1185.

[2] *Gazzetta*, 22, i. p. 250. J.C.S. Ab's. vol. 62, 1892.

[3] *Journal of the Society of Chemical Industry*, 1909, 28, p. 268.

[4] *Proceedings of the Royal Society*. 1889, xlvi., p. 216.

Two or more of these products are always formed when iron is dissolved in nitric acid; the mixture ascertained by analysis

	Cubic Centimetres.	Iron-equivalent of 1·0 cc. of Gas.
Nitrogen peroxide . .	1200	0·00083 gm.
Nitric oxide . .	400	0·00250 ,,
Nitrous oxide. . .	150	0·00666 ,,
Nitrogen . . .	120	0·00833 ,,
Ammonia . . .	150	0·00666 ,,

must then fulfil the condition that the total iron-equivalent of its constituents shall be equal to the amount of iron used. If this is not the case it is a sure indication either of an error in the analysis or of the presence of an undetected product of the reduction.

(1.) *The Estimation of NO, N_2O, N_2, and NH_3 formed on dissolving Iron in Nitric Acid.*

The type of vessel in which the sample is dissolved is shown in Fig. 1, A, B. The capacity of the bulb A is about 40 cubic centimetres; its volume, together with that of the narrow exit tube C, is accurately determined by filling with water. The vessel having been dried, 0·3 gramme of sample is placed in A and the exit tube is attached. The vessel is then connected with a Tate's air-pump through E (Fig. 2), by which the bulb A is exhausted. Stopcock 1 is next closed and stopcock 2 opened, which allows pure nitrogen from the gas-holder F to enter the vessel. The rubber connection D is now removed from the supply tube and attached to the graduated gas-receiver G, as shown in Fig. 1, being kept closed with the fingers during the transfer. Tap 3 is then opened for a second or so to allow the excess nitrogen to escape and to bring the remaining gas to atmospheric pressure. It need scarcely be remarked that the bulb A should not be warmed by the hand during these operations. The required amount of nitric acid is now measured and placed in the tube B; stopcock 4 is opened and a little nitrogen drawn over into the receiver G by slightly lowering the mercury-holder K. The acid is then admitted by stopcock 3 and the bulb A is at once immersed in the boiling water contained in the basin. Care must, of course, be taken to prevent the entrance of any air into A when the acid is admitted. As the reaction proceeds the vessel K is lowered so as to keep the mercury below the level of that in G. When the reaction is completed, the boiling is continued for a short time while the pressure is lowered a few inches, especially when using weaker acids, to complete the expulsion of the gases from the solution in A. The tube B is then filled with distilled water, and, after ensuring that the mercury-holder K is sufficiently lowered, tap 3 is opened and the residual gas in A is rapidly driven over by the water into the gas-receiver G. When the water reaches D, the taps are closed and the apparatus A, B, is detached. The gas-receiver G contains over the mercury a small depth of water on which rests a layer of liquid paraffin : it is now shaken gently, the gases being kept under a low pressure ; by this means any nitrogen peroxide which may be present is quickly condensed on the wet sides of the vessel and the gases become colourless. After waiting for a short time, to ensure that the gases are at room-temperature, the mercury is levelled and the

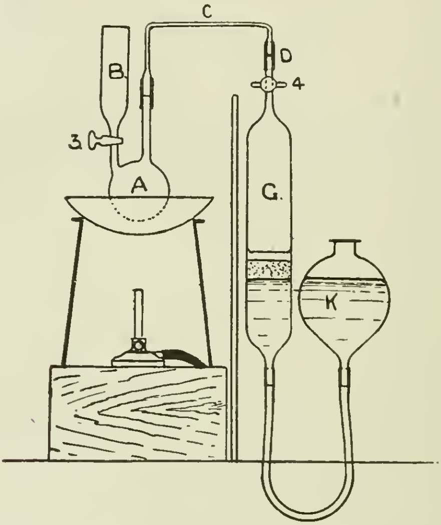

FIG. 1.—Apparatus employed for dissolving Samples and collecting the Gases.

gas-volume is read. The liquid paraffin is used to prevent the removal, on standing, of any of the nitric or nitrous oxide by solution in the water.

Analysis of the Gases.—The analysis of the gases is conveniently made in a Stead's apparatus. A suitable amount of the sample is transferred to the eudiometer tube and the following solutions are used, in the order given, as absorbents for the different constituents.

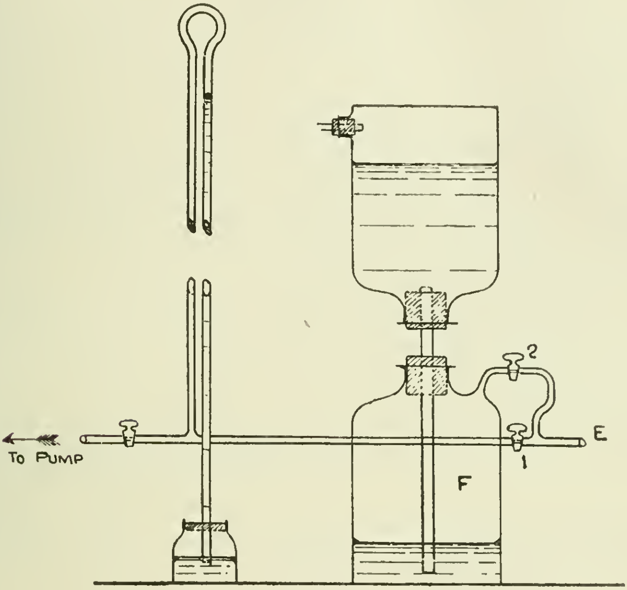

Fig. 2.—Gauge and Nitrogen-Holder for filling Apparatus.

(*a*) Nitric oxide. A solution of potassium permanganate made by dissolving 20 grammes in 450 cubic centimetres of distilled water and adding 50 cubic centimetres of dilute sulphuric acid (1 : 3 aq. by vol.). This solution is held in a 50 cubic centimetre separating funnel (pear-shaped pattern), which can be attached to the exit tube of the eudiometer and removed when not in use. The measured sample is transferred to the funnel, which is then gently shaken ; the absorption is complete in about thirty seconds, as can be seen by the persistence of the violet tint on the sides of the apparatus. The amount of nitric oxide present is calculated from the volume-difference.

(*b*) Nitrous oxide. Methylated spirit is used to absorb this gas. It is convenient to have the Stead's absorption tube expanded into a bulb at the top and narrowed considerably below so that the liquid can be well shaken. The absorption is rather slow and not quite complete ; fortunately the amount of nitrous oxide present is always small, being at most 6 per cent. of the total gases. The methylated spirit can therefore be used repeatedly.

(*c*) Carbon dioxide. This gas, when present, is absorbed in a strong solution of potassium hydrate.

(*d*) Oxygen (and alcohol vapour). After the removal of the nitrous oxide (or carbon dioxide), the gas is passed into a tube containing an alkaline solution of pyrogallic acid of the usual strength to absorb slight amounts of oxygen which are sometimes introduced during the absorption of the nitric oxide.

The different constituents having thus been removed, the amount of nitrogen present can be ascertained from the volume of the residual gas.

Estimation of the Ammonia.—The evolved gases were several times tested for ammonia, but no appreciable amount was ever found to be present in them ; the whole of the ammonia formed in the reaction is, therefore, held by the acid in the bulb, and can be estimated by distilling with caustic hydrate in the usual way. The following solutions are required :

1. Strong solution of sodium hydrate containing 600 grammes per litre.
2. Standard solution of sulphuric acid, 1·0 cubic centimetre of which will neutralise 1·0 cubic centimetre of gaseous ammonia at 0° C. and 760 millimetres pressure. 100 cubic centimetres of this solution is therefore neutralised by 0·237 gramme of pure dry sodium carbonate.

The distillation can be made in a conical flask of about 600 cubic centimetre capacity. The flask is fitted with a rubber cork, through which pass (1) a tap-funnel ; (2) an exit tube leading to a Davies condenser ; (3) a syphon tube by means of which the contents of the flask can be quickly removed without disconnecting the apparatus. This arrangement is especially convenient when a large number of estimations are being made. About 300 cubic centimetres of water are placed in the flask with 5 cubic centimetres of the sodium hydrate solution ; the mixture is boiled until the distillate remains colourless after the addition of a few drops of phenolphthalein solution. The contents of the bulb are then added to the flask, and the distillation is continued until about 100 cubic centimetres have passed over. A few small pieces of silica brick in the flask serve to prevent any violent ebullition. The distillate is titrated with the standard sulphuric acid solution ; lacmoid is used as a final indicator, the end point being shown by the change in colour from blue to pink.

Notes and Precautions.—1. The nitric acid used in this investigation was not specially purified, the solutions of different strengths being made from colourless acid (sp. gr. 1·40) of the quality usually supplied for analysis. The difficulty in starting the reaction, which was observed by Veley when using acid entirely free from nitrous acid, was not encountered.

2. The acid-strengths employed are given in the table below. Intermediate strengths, when required, were obtained by mixing accurate proportions of these acids ; in referring to the acids the concentration given is always the mass per 100 cubic centimetres, as given in the fourth column.

TABLE I.—*Showing various Strengths and Amounts of Nitric Acid used.*

	Specific Gravity.	Approx. Amount of HNO_3 (1·4) taken to make 100 c.c.	Weight of HNO_3 in Grammes per 100 c.c.	Volume used in Test.
		Cubic Centimetres.	Grammes.	Cubic Centimetres.
1	1·06	12·5	11·5	20·0
2	1·115	20·0	21·5	11·0
3	1·145	25·0	27·5	8·5
4	1·175	33·0	33·5	7·0
5	1·20	40·0	39·0	6·0
6	1·255	50·0	51·0	4·6
7	1·29	60·0	59·5	4·0
8	1·33	70·0	69·7	3·5

3. In making a test, care must be taken to dry the tube B (Fig. 1), and to drain thoroughly the bulb A before starting.

The dilution of the acid used with even 0·1 cubic centimetre of excess water is sufficient in some instances to cause an appreciable divergence from the true result.

4. A slight error probably arises from the solution of nitric oxide in the water used to expel the gases from the bulb; the time of contact is very short, and experiment showed that this loss was negligible.

5. The permanganate employed for the absorption of nitric oxide should be of good quality, and the prepared solution must not evolve gas on standing; this difficulty can usually be avoided by boiling the solution for a few minutes. Chlorides must be carefully excluded, and the eudiometer should accordingly be washed out when needed with very dilute sulphuric acid. Very strong solutions of the salt are apt to liberate rather large amounts of oxygen during the absorption; the 4 per cent. solution used was found to work very satisfactorily.

6. The amount of nitrogen evolved during the reaction is obtained after deducting the volume used to fill the apparatus from the total volume found; great care should therefore be used in filling the bulb, since any error at this stage is thrown on to the small quantity of residual nitrogen.

7. When drillings are dissolved the reaction may be violent, especially with the stronger acids; in such cases it is well to reduce the pressure of nitrogen in the apparatus as far as possible before admitting the acid.

8. The pure nitrogen required to fill the bulb can readily be prepared by burning phosphorus in a bell-jar over water and drawing the residual gas into a gas-holder (as shown in Fig. 2, F) containing alkaline pyrogallol. A layer of liquid paraffin is placed in the upper vessel to prevent contact with air. In this way one litre of strong pyrogallol will serve to prepare many litres of nitrogen.

Example.—The following is given as an example of a typical determination by this method, and shows how the iron-equivalent is obtained from the gas analysis:

Weight of sample taken, 0·30 gramme. Volume of apparatus, 43·0 c.c. Temperature 25° C. Pressure, 750 mm. Acid strength, 33·5 grammes per 100 c.c. Gas-volume 141 c.c. (after removal of NO_2).

Amount taken for analysis, 256.	Difference.
89 (permanganate)	167
86 (alcohol)	3
84 (pyrogallol)	2

Composition of the gas calculated from the above figures:

Nitric oxide . .	92·0 c.c.	= at N.T.P. 83·1 c.c. ;	iron-equivalent, 0·208 gramme
Nitrous oxide . .	2·5 ,,	= ,, 2·5 ,,	,, 0·017 ,,
Nitrogen . .	46·2 ,, (less 43·0 c.c.)	= ,, 3·0 ,,	,, 0·025 ,,
Ammonia (titrated)	6·1 c.c.	= ,, 6·1 ,,	,, 0·041 ,,
			0·291 ,,

After correcting for temperature and pressure there is thus 0·01 gramme of iron not accounted for; this deficiency is chiefly due to the formation of a small volume of nitrogen peroxide which was not estimated. It will be seen on reference to the table on p. 8 that the amount of iron equivalent to 1 cubic centimetre of this gas is much less than that represented by an equal volume of the other products. A considerable quantity of the gas must therefore be produced before the total iron-equivalent obtained is seriously affected by its omission; the presence of as much as 30 cubic centimetres would only cause a deficiency of 0·025 gramme. With acid-strengths below 40 per cent. this amount is seldom formed, and as these were the strengths chiefly required in the present investigation, the estimation of the nitrogen peroxide, which would greatly complicate the method of analysis, has been omitted.

In order to verify the accuracy of the method, mixtures similar in composition to those given by iron were made up from samples of the pure gases. The results of analyses of these mixtures are given in Table II., and are, for the present purpose, in sufficiently close agreement with the quantities taken.

TABLE II.

	NO.	N_2O.	N_2.
Mixture .	100	10	64
Analysis .	99	9·5	66
Mixture .	85	10	59
Analysis .	84	9·5	60

(2.) *Variation in the Reaction of Pure Iron with different Acid-Strengths.*

The method of analysis having been described, the variations in the composition of the gases which are obtained on dissolving a pure iron in different strengths of nitric acid will now be considered. The results yielded by sample 3 (Table XI.) can be given as a typical illustration. A piece of this material was first heated at 1000° C. for one hour and then slowly cooled in the furnace. Small portions were next cut from it with a fine saw, and these were filed down until the weight of each was 0·3 gramme. Every care was taken in filing to prevent any appreciable amount of deformation of the pieces by cold-work ; the small file used was applied lightly, so that only the skin of the samples would be altered to any extent. The preparation of cut unstrained pieces was made in this way throughout the investigation ; the results obtained from such pieces are practically the same as those given by cut samples which have been reduced to the correct weight by the action of acid.

The analyses of the gases evolved when these pieces were dissolved at 100° C. in the various strengths of acid are given in Table III. ; the usual quantities of the reagent, shown in Table I., were taken.

The gradual decrease in the total iron-equivalent as a stronger acid is used is due to the formation of increasing quantities of nitrogen peroxide. The presence of this gas is readily detected by its red colour, and a rough estimate of the amount formed can thus be obtained. As the acid-strength is raised, iron and steel samples invariably yield increasing amounts of the peroxide on dissolving. In the above example the gases liberated with acid below 24 per cent. were practically colourless, so that only a trace of nitrogen peroxide could have been produced. The fact that, in such cases, the total iron-equivalent obtained by calculation from the equations (p. 2) so closely agrees with the amount of sample used is, therefore, very strong evidence that these formulæ correctly represent the final products of the reactions which take place.

The results given in Table III. are also shown in Fig. 3, in which the iron-equivalents of the different products have been plotted above one another as ordinates and the acid-strengths as abscissæ. The most striking feature is the sudden change in the nature of the reaction at acid-strength 24. With weaker acids nearly two-thirds of the iron reacts to produce ammonia and nitrogen ; with stronger acids more than two-thirds of the metal yields only

TABLE III.

Acid-Strength (gms. per 100 c.c.)	11·5.	21·5.	22·7.	23·9.
Nitric oxide	32·0 c.c. = 0·080 gm.	39·0 c.c. = 0·098 gm.	41·0 c.c. = 0·102 gm.	49·0 c.c. = 0·122 gm.
Nitrous oxide	2·5 ,, = 0·017 ,,	2·5 ,, = 0·017 ,,	2·0 ,, = 0·013 ,,	2·0 ,, = 0·013 ,,
Nitrogen	13·0 ,, = 0·108 ,,	8·0 ,, = 0·067 ,,	8·0 ,, = 0·067 ,,	8·2 ,, = 0·068 ,,
Ammonia	14·0 ,, = 0·093 ,,	18·2 ,, = 0·121 ,,	18·3 ,, = 0·122 ,,	14·1 ,, = 0·094 ,,
Total gas volume at N.T.P.	47·5 c.c.	49·5 c.c.	51·0 c.c.	59·2 c.c.
Total iron-equivalent	0·298 gm.	0·303 gm.	0·304 gm.	0·297 gm.
Acid-Strength (gms. per 100 c.c.)	**25·1.**	**26·3.**	**27·5.**	**33·5.**
Nitric oxide	74·0 c.c. = 0·185 gm.	83·0 c.c. = 0·207 gm.	87·0 c.c. = 0·218 gm.	90·0 c.c. = 0·225 gm.
Nitrous oxide	2·5 ,, = 0·017 ,,	2·5 ,, = 0·017 ,,	2·5 ,, = 0·017 ,,	1·5 ,, = 0·010 ,,
Nitrogen	5·5 ,, = 0·046 ,,	5·8 ,, = 0·048 ,,	4·3 ,, = 0·036 ,,	3·5 ,, = 0·029 ,,
Ammonia	5·6 ,, = 0·037 ,,	3·0 ,, = 0·020 ,,	2·0 ,, = 0·013 ,,	1·0 ,, = 0·007 ,,
Total gas volume at N.T.P.	82·0 c.c.	91·3 c.c.	93·8 c.c.	95·0 c.c.
Total iron-equivalent	0·285 gm.	0·292 gm.	0·284 gm.	0·271 gm.

nitric oxide. The curve *a, b, c* expresses this remarkable characteristic, and similar features are to be found in the reaction of nitric acid with all iron and steel samples. The exact strength of acid at which this change occurs varies widely with different samples, and the present investigation deals chiefly with the influence of mechanical deformation on the position and shape of this characteristic curve, which will be termed the "*reaction-curve*" of the sample.

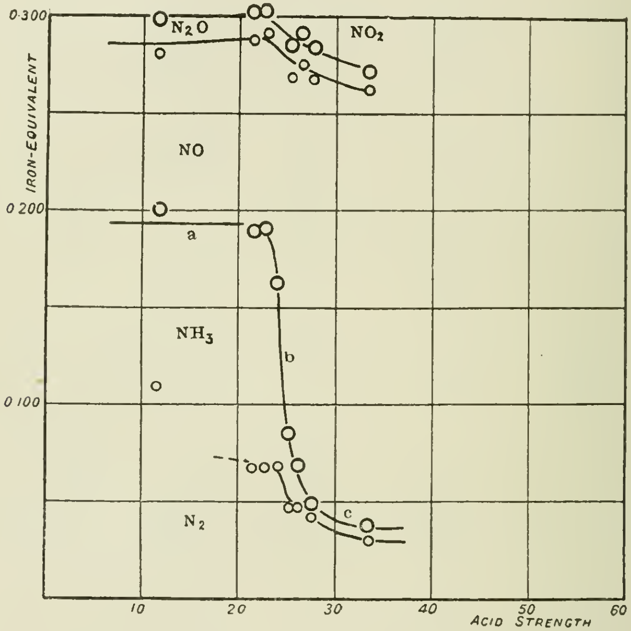

Fig. 3.—Reaction of Pure Iron with Nitric Acid.

Influence of an Excess of Acid.—It will be seen from the equations (p. 2) that the total quantity of nitric acid consumed (neutralised and destroyed) in dissolving 0·3 gramme of iron depends upon the composition of the gases which are formed. The actual quantities of acid required to yield the different products have been calculated and are given in the following table :

TABLE IV.—*Showing the Quantity of* HNO_3 *consumed in dissolving* 0·3 *gramme Iron in* 2·34 *gms. of the Acid.*

Gas.	Nitric Acid Destroyed. Grammes.	Percentage Destroyed.	Total Acid Consumed. Grammes.	Percentage Consumed.
NO_2	1·012	43·0	2·025	86·0
NO	0·337	14·5	1·350	58·0
N_2O	0·253	10·8	1·265	54·0
N_2	0·202	8·6	1·215	51·6
NH_3	0·126	5·4	1·139	48·6

The greatest amount would be consumed if nitrogen peroxide alone were produced, and is equivalent to 5·2 cubic centimetres of 1·2 acid. The quantity of this acid used in the method given on p. 3 is 6·0 cubic centimetres, and the other acid-strengths are taken in proportional amounts, so that an equal weight of nitric acid (2·34 grammes) is employed in all cases. The quantity taken is thus a little in excess of that required to complete the reaction, no matter which product is formed. It is clear also that as the reaction proceeds the amount of free acid present is greatly reduced, while the ferric nitrate accumulates, and it would seem at first sight almost essential to use a large excess of nitric acid, so as to diminish this variation in the acid-strength as much as possible. In order to examine the effect of dissolving in larger amounts of acid, two sets of experiments were made, in which the quantity of sample (sample 2, Table XI.) was kept constant (0·3 gramme) while the quantities of the acid selected were increased as far as the capacity of the apparatus would permit.

The results of these experiments are plotted in Figs. 4 and 5, in which the number of cubic centimetres of acid taken is measured by the abscissæ, while the iron-equivalents of the various gases formed are plotted one above another as ordinates. The total iron-equivalent yielded by the analysis is, therefore, represented by the top line, and it will be seen that as the quantity of acid was increased this total equivalent gradually diminished; at the same time there was a diminution in the quantities of both nitric oxide and ammonia and an increase in that of nitrogen. The cause of these variations will be discussed later; for the present purpose it is sufficient to note that the uniformity in results which might have been expected owing to the presence of larger, and therefore less variable, amounts of free acid was not obtained.

The results plotted in Fig. 3 show clearly that the reduction products formed in the reaction may differ greatly even with relatively slight changes in the concentration of nitric acid employed. Now if the nature of the reaction was entirely dependent upon the amount of free acid present, then, with the small quantities of acid used, no sharp curve such as *a, b, c*, Fig. 3, could possibly be obtained, since each result would be the average over a considerable range of free-acid concentration. For example, by the time the metal had dissolved in the 7·0 cubic centimetres of 33·5 acid-strength used (Fig. 3) the acid-strength had been reduced to about acid-strength 13·5 ; the greater part of the reaction must consequently have taken place with an acid-strength which, in the absence of nitrate, would have yielded chiefly nitrogen and ammonia with this particular sample, and

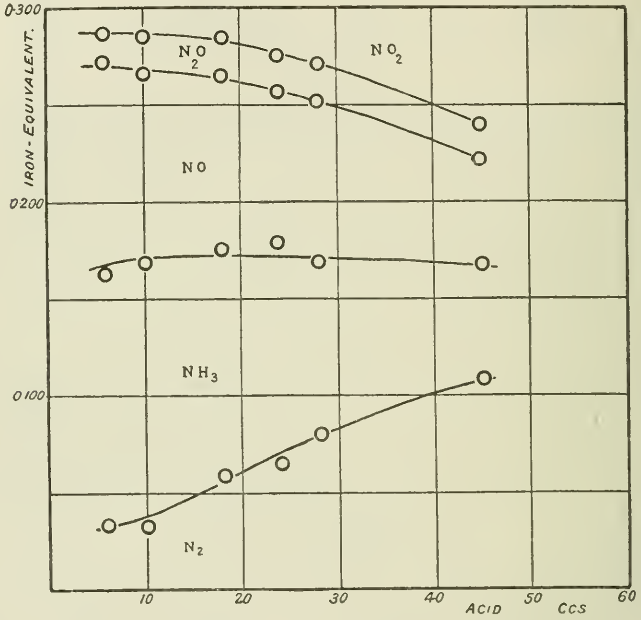

FIG. 4.—Effect of Increasing Amounts of Nitric Acid (27·5 gms. per 100 c.c.).

yet the amount of these products is very low. The fact that such a sharp curve is found must therefore be taken as proof that the reaction is not determined simply by the acidity. The only other quantity involved is the concentration of the group NO_3, and, unlike the free acid, this quantity usually remains approximately constant throughout the reaction. At the end of the process the group NO_3 is present partly as ferric nitrate and partly as free acid. Thus there seems to be no alternative to the view that the products of the reaction of iron with nitric acid depend not simply upon the acidity, but upon the concentration of the group NO_3, present either as free acid or as ferric nitrate.

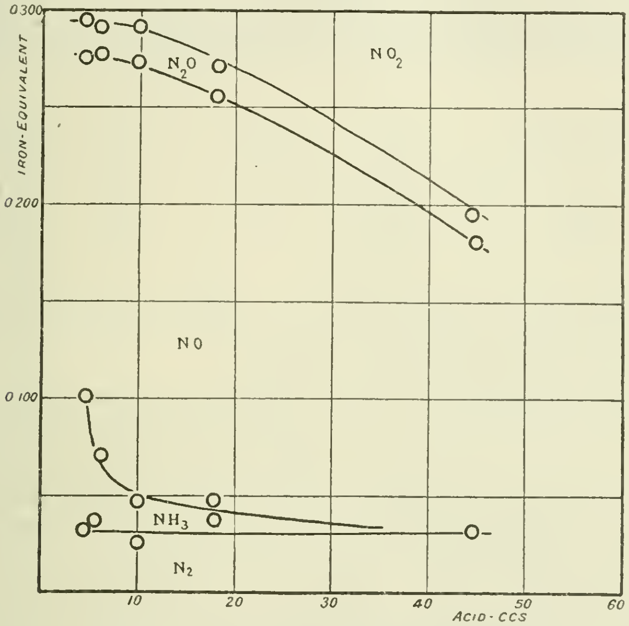

FIG. 5.—Effect of Increasing Amounts of Nitric Acid (37 gms. per 100 c.c.).

In connection with the above conclusion, the following experiment affords an interesting example of the influence exerted upon the reaction by the concentration of the NO_3 group. Seven cubic centimetres of nitric acid (acid-strength 36) were partly neutralised by dissolving 0·15 gramme of pure iron, and the gases formed were expelled by boiling for a short time. The amount of acid destroyed, calculated from the composition of the evolved gas by means of Table IV., is such that the concentration of NO_3 was reduced to an amount corresponding with acid-strength 33·5, while the free acid-strength was reduced to 26. The acid thus prepared was now used to dissolve, at 100° C., 0·30 gramme of a sample of iron, the gases being estimated in the usual way. The result is shown below, together with those given by the same sample when dissolved in 7 cubic centimetres of acid-strength 33 and in 8·5 cubic centimetres of acid-strength 26.

Acid-Strength.	NO.	N_2O.	N_2.	NH_3.
7 c.c. of 36 + 0·15 gr. Fe	85·5	1·5	2·9	6·8
7 ,, 33·5	86·0	1·5	2·2	6·4
8·5 ,, 26	55·0	3	4·5	15·5

Clearly the fact that in the first instance much of the NO_3 was present as iron nitrate, and not as free acid, has made no appreciable difference in the reaction.

The formation of the various reduction products involves the loss of a certain amount of NO_3 during the reaction ; the equivalents of this in nitric acid consumed in the formation of the different gases when using 0·3 gramme of iron are given in Table IV. The total concentration of NO_3 is therefore diminished somewhat during the reaction, while the proportion present in the form of ferric nitrate increases. On consideration, it is clear that the effect of such variations in the concentration of the NO_3 must always be to make the sharp change in a curve such as *a*, *b*, *c*, Fig. 3, less pronounced. The true curve, if these variations could be avoided, should, therefore, be even steeper than that obtained with the quantity of acid used in the method.

In order to find whether an excess of acid would really yield a steeper curve, experiments were made in which four times the quantity of acid normally used was taken to dissolve the sample.[1] The variation in the concentration of NO_3 through reduction was thereby greatly minimised. The acid was added hot ; and in each case the ammonia was re-distilled (p. 20). The results are

[1] In order to keep the quantity of acid as small as possible, a sample of mild steel plate was taken for which the critical change in reaction took place at a fairly high acid-strength.

plotted in Fig. 6, curve A; curve B is that obtained from the same sample when dissolved in the usual amount of acid. The difference between the two curves is that which would be anticipated from the foregoing considerations, the curve given by the excess acid is steeper and lies to the left of the other, the two curves converging at the top. It should be observed here that, since nitrogen peroxide is invariably produced in increasing amounts as the acid-strength is raised, curves obtained by the method (p. 3) which lie further toward the right can never be so steep as those which lie between acid-strengths 18 and 25, because the formation of nitrogen peroxide involves the reduction of a greater amount of the NO_3 group.

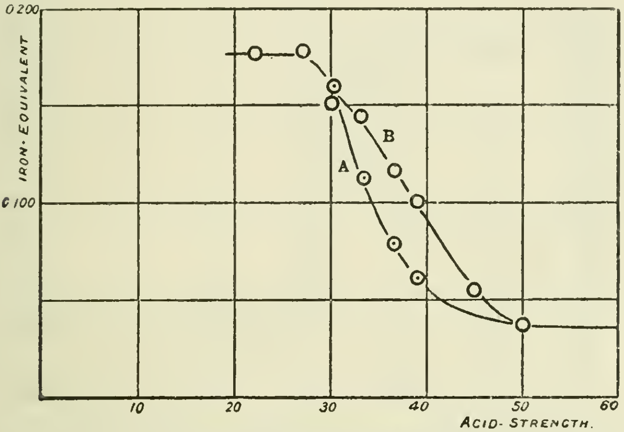

FIG. 6.—Reaction-Curves of same Sample: A, with four times the usual amount of acid; B, with usual amount of acid.

It is thus evident that the curves are not so steep as they would be if the concentration of the NO_3 could be kept quite constant. In the case of the curve *a, b, c,* Fig. 3, at a certain acid-strength (24) the nature of the reaction of the iron sharply changes, and, if due allowance could be made for the effect of variations in the concentration of the NO_3, there is strong reason to believe that the true curve would be discontinuous. With other samples of pure annealed iron a similar effect is to be observed.

Influence of Temperature on the Reactions.—In all the foregoing experiments the iron was dissolved at 100° C. Some similar tests were next made by immersing the bulb in water at 45° C. and dissolving the metal as nearly as possible at that temperature. When the action had ended, the solutions were heated at 100° C. to expel the nitric oxide before making the gas analysis. The results of two sets of tests on different samples of pure iron are plotted in Figs. 7 and 8; the results obtained by dissolving the same material at 100° C. are also shown for comparison.

The "reaction-curve" is but little altered, an important property, since it is sometimes difficult to ensure solution entirely at 100° C. in the ordinary method. The nitrogen formed, especially with the acids of lower concentration, was considerably in excess of that obtained at 100° C. This increase had, however, taken place largely at the expense of the ammonia. The chemical reactions involved will be discussed later (p. 20); it will suffice at present to remark that small temperature variations such as may occur in practice have a negligible influence on the "reaction-curve."

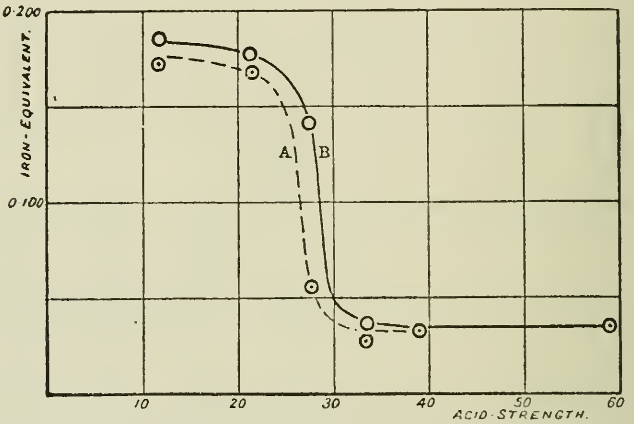

FIG. 7.—Reaction-Curves of Pure Iron dissolved: (A) at 100° C.; (B) at 45° C.

Influence of Pressure on the Reactions.—In cases where hydrostatic pressure has been shown to influence the course of a reaction, the pressure required to produce an appreciable effect is often measurable in atmospheres. In the method as given on p. 3 the reaction always takes place at a pressure only a little below atmospheric, and such effects are therefore scarcely to be expected. Some experiments were made, however, in which a sample was dissolved, (*a*) at a pressure about 500 millimetres of mercury above atmospheric, (*b*) at a pressure about 200 millimetres below atmospheric; the same acid-strength being used in each case. It will be sufficient to record that no appreciable variation was observed.

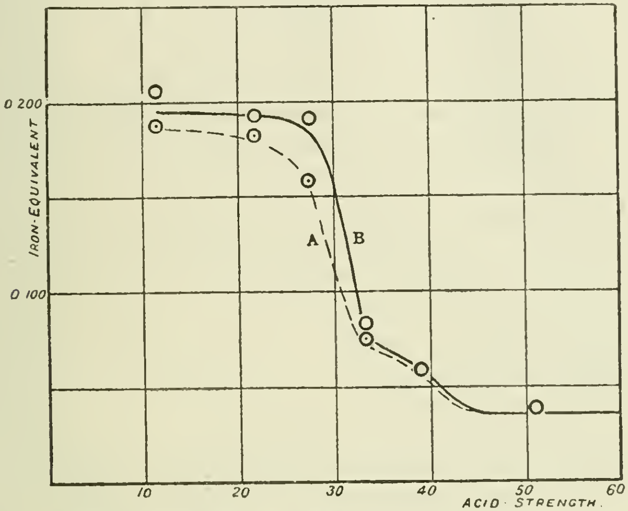

FIG. 8.—Reaction-Curves of Pure Iron (sample 2, Table XI.) dissolved: A, at 100° C.; B at 45° C.

(3) *Chemical Reactions Involved.*

(*a*) *Solubility of Nitric Oxide in Nitric Acid.*—It has been shown by Veley[1] that when nitric oxide at atmospheric pressure is passed into nitric acid, nitrous acid is formed according to the equation:

$$2NO + HNO_3 + H_2O \rightleftarrows 3HNO_2.$$

Equilibrium between the nitric and nitrous acids is attained when ther atio of the latter to the former is about 1 : 10, this proportion depending on the temperature.

In the present method, if the full iron-equivalent is to be obtained, it is essential to secure the complete removal of dissolved nitric oxide before distilling the solution for ammonia.

[1] *Proceedings of the Royal Society*, 1892, vol. lii. p. 27.

If by any chance some nitric oxide is retained, then, on adding the nitric acid solution to the boiling soda, nitric oxide is not always held as nitrite, but may be expelled and oxidised to nitrogen peroxide in the condenser, yielding nitric and nitrous acids in the distillate ; this effect was chiefly observed in experiments where large amounts of acid were used. Thus the presence of nitric oxide in the solution leads sometimes to the anomalous result that the distillate from a strongly alkaline solution is first acid and subsequently on evolution of the ammonia becomes alkaline. By returning the distillate to the flask and re-distilling a correct value for the ammonia is obtained.

It is this solubility of nitric oxide in nitric acid which is the chief cause of the low total iron-equivalents which result from using excess of acid as shown in Figs. 4 and 5 ; with the restricted amount of nitric acid used in the method, practically all the nitric oxide is evolved in a few minutes at 100° C. under slightly reduced pressure. The completeness of the expulsion of this gas suggests that the cause does not lie simply in the small quantity of nitric acid employed. In an experiment in which some very strong iron nitrate solution was added to a sample dissolved in a large excess of acid, the nitric oxide gas held in the solution was found then to be freely evolved. Thus the iron nitrate seems to facilitate the expulsion of nitric oxide, and it is probably owing to the large concentration of iron nitrate in the solution that the complete estimation of the nitric oxide formed is possible under the conditions of the method.

(*b*) *Formation of Secondary Nitrogen from Ammonia.*—The results mentioned on p. 18 showed that, on dissolving samples at 45° C. and afterwards boiling the solutions, more nitrogen and less ammonia were formed than on dissolving at 100° C. in the same acid. This interchange of ammonia and nitrogen can readily be explained on the assumption that combination occurs between the ammonia and nitrous acid formed during the reaction at 45° C., and that the ammonium nitrite so produced decomposes at a higher temperature, yielding nitrogen, according to the equation :

$$NH_4NO_2 = N_2 + 2H_2O.$$

The formation of a greater amount of ammonium nitrite at the lower temperature is due to the retention of some of the nitric oxide in the solution; in dissolving at 100° C. this gas is swept away too quickly to allow the same combination with ammonia to take place.

Further evidence in this direction is yielded by the following experiments: 0·3 gramme portions of annealed iron (sample 2, Table XI.) were dissolved, (*a*) at 45° C. without subsequent boiling; (*b*) at 45° C. with subsequent boiling, and the gases evolved were analysed. In order to avoid error from the retention of nitric oxide in the solution, the ammonia was re-distilled in all these experiments. The results are given in the following table:

TABLE V.—*Gases Evolved on Dissolving at* 45° *C. with and without subsequent Boiling.*

Acid Used. Grammes per 100 c.c.		NO.	N_2O.	N_2.	NH_3.	Iron Equivalent.	
						Total.	N_2+NH_3.
27·5	Not boiled	15·0 c.c.	3·0 c.c.	4·3 c.c.	19·0 c.c.	0·221 gm.	0·163 gm.
	Boiled	30·7 ,,	3·5 ,,	16·0 ,,	9·0 ,,	0·293 ,,	0·193 ,,
	Difference	15·7 c.c.	...	11·7 c.c.	10·0 c.c.		
33·5	Not boiled	61·0 c.c.	2·0 c.c.	2·5 c.c.	6·5 c.c.	0·229 gm.	0·064 gm.
	Boiled	80·0 ,,	2·5 ,,	7·5 ,,	1·8 ,,	0·291 ,,	0·074 ,,
	Difference	19·0 c.c.	...	5·0 c.c.	4·7 c.c.		

The low total iron-equivalents given by the samples not boiled are due to the retention of nitric oxide in the solution. The most striking feature in these results is the great increase in the nitrogen from the boiled tests, which has evidently occurred at the expense of the ammonia. According to the above equation, the formation of one volume of this secondary nitrogen involves the destruction of the same volume of ammonia; as will be seen in the table, the actual differences in the amounts of these two products are closely in agreement with those required by the equation. The slightly lower ammonia differences are probably due to the destruction of a little of the ammonium nitrite present in the unboiled solutions by a momentary occurrence of the same reaction when these solutions are added to the boiling alkali. That ammonium nitrite does yield nitrogen in the conditions of the test can be directly proved by adding a nitrite. For example, 0·3 gramme of a pure iron was dissolved in 6 cubic centimetres of nitric acid (1·2) and the solution boiled to expel all gases. On cooling, small quantities of potassium nitrite and ammonium nitrate were added to the liquid, which was then placed in the apparatus. The gases evolved on heating for a few minutes at 100° C. were collected and analysed; 14·0 cubic centimetres of nitrogen were found to have been liberated.

Again, a similar result was obtained by the addition of ammonium nitrate alone to the acid (1·2) before dissolving, thus:

	NO.	N_2O.	N_2.
Normal result at 100° C. . .	91·0 c.c.	2·0 c.c.	3·0 c.c.
Addition of 0·5 gramme NH_4NO_3	80·0 ,,	2·0 ,,	18·0 ,,
Difference . . .	11·0 c.c.	...	15·0 c.c.

The additional ammonia reacts with the nitrous acid present, and yields nitrogen, according to the following equations:

$$\begin{aligned} 2NO + HNO_3 + H_2O &= 3HNO_2 \\ 3HNO_2 + 3NH_3 &= 3NH_4NO_2 \\ 3NH_4NO_2 &= 3N_2 + 6H_2O \end{aligned}$$

Thus, three volumes of ammonia and two of nitric oxide are required to form three volumes of nitrogen, a ratio closely agreeing with that obtained in the above experiments.

These experiments make it clear that considerable amounts of nitrogen can be produced by reactions in the solution after the sample has dissolved. This nitrogen is therefore not one of the primary reaction products of the solution of iron in nitric acid, and is termed secondary nitrogen throughout this Report, the word "primary" being used to indicate those substances which appear to be initially formed.[1] The effect of the formation of additional amounts of secondary nitrogen is seen in the curves plotted in Figs. 7 and 8; the slight shift of the curves to the right, caused by dissolving at 45° C., can be explained as partially due to the transformation, at the lower temperature, of part of the nitric oxide to nitrogen, according to the above equations, so that the total iron-equivalent of the ammonia and nitrogen is higher than that found on dissolving at 100° C.

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[1] This distinction has been made by Divers, *Journal of the Society of Chemical Industry*, 1904, 23 (24), 1182–1186.

A few experiments were also made in order to ascertain the influence of the temperature of solution upon the ratio of nitrogen to ammonia obtained. The results given by a sample of pure iron dissolved at 45°, 60°, 80°, and 100° C. in acid-strength 27·5 are shown in Fig. 9; in each case the solution was boiled after the sample had dissolved.

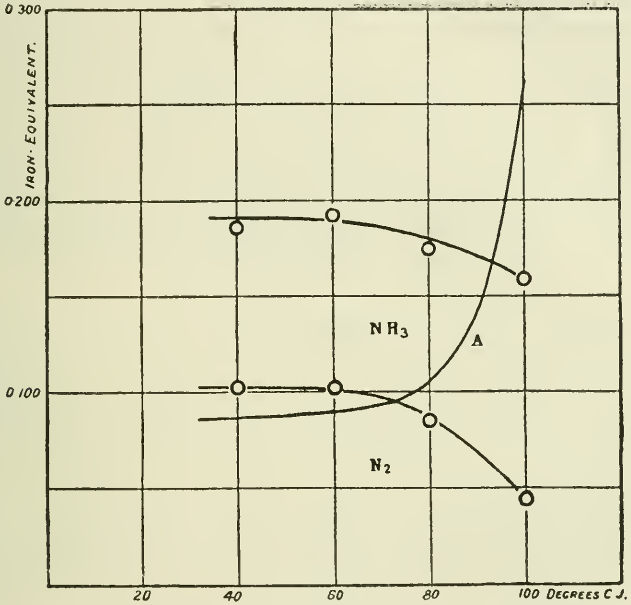

Fig. 9.—Nitrogen and Ammonia evolved from Iron dissolved at various Temperatures. A: Ratio of ammonia to nitrogen.

The line A shows the ratio of the ammonia-equivalent to the nitrogen-equivalent, and it is clear that when the temperature of solution rises above 80° C. there is a rapid diminution in the amount of secondary nitrogen formed. This rapid change in the neighbourhood of 100° C., which coincides with a more vigorous evolution of the gases, indicates that the fall in secondary nitrogen is due to the nitric oxide being driven from the solution before reaction with ammonia can occur. For this reason the temperature of 100° C., in dissolving the sample, is to be preferred, since the formation of secondary nitrogen, which involves a diminution in the nitric oxide, is thereby reduced to a minimum.

(*c*) *Formation of Nitrogen Peroxide.*—It has already been remarked that deficiencies in the total iron-equivalents given by the method of analysis employed are due to the formation of nitrogen peroxide, which is not estimated. The quantity of this gas formed invariably increases with the acid strength used; an instance is seen in the fall of the total equivalent plotted in Fig. 3. The formation of nitrogen peroxide is diminished, however, by lowering the temperature of solution; in many cases, samples which gave a red gas at 100° C. gave almost colourless gas at 45° C. even when the solution was boiled after the sample had dissolved. The following examples show the changes which can be thus produced in the composition of the evolved gases:

TABLE VI.

Acid-Strength. Gms. per 100 C.C.	Temperature of Dissolving.	NO. C.C.	N_2O. C.C.	N_2. C.C.	NH_3. C.C.	Fe-eq.	Approx. NO_2 (by difference). C.C.
51	100° C.	63·0	3·0	7·5	4·0	0·268 gm.	39·0
	60° C. and boiled	71·5	3·0	7·5	3·5	0·285 ,,	18·0
65	100° C.	53·5	2·5	4·5	1·8	0·201 gm.	119·0
	60° C. and boiled	81·0	2·5	4·5	1·2	0·265 ,,	42·0

It is evident that the variations in nitric oxide are due to an interchange between this gas and the nitrogen peroxide, for the quantities of the other gases formed at the two temperatures do not differ appreciably. The conditions governing the exchange between these oxides of nitrogen are probably very complicated; in the absence of reactions between these and other products, the interchange of the two products can be represented by the following equations:

$$(a)\ 2NO_2 + H_2O = HNO_3 + HNO_2$$
$$(b)\ 3HNO_2 = HNO_3 + 2NO + H_2O.$$

Thus three volumes of nitrogen peroxide can be formed in place of one volume of nitric oxide. The ratio in which these gases are actually obtained will depend upon the temperature of solution, acid-strength, and other conditions of the test.

(*d*) *The Formation of Nitrous Oxide.*—At 100° C. this gas is always formed in very small amounts. The experiment given on p. 22 proves that it is not produced by the decomposition of ammonium nitrate present in the solution, although it is often prepared for laboratory purposes by heating the anhydrous salt. It is probable that the nitrous oxide present in the gases arises from the decomposition of a small amount of hydroxylamine, according to the following equations:

$$\begin{aligned} NH_2OH + HNO_2 &= H_2N_2O_2 + H_2O \\ H_2N_2O_2 &= N_2O + H_2O. \end{aligned}$$

It should be observed in this connection that hydroxylamine may also possibly yield nitric oxide by decomposition of the nitrate, according to the equation:

$$NH_2OH \cdot HNO_3 = 2NO + 2H_2O.$$

Thus it is possible that both nitric and nitrous oxides are really secondary products of the rapid decomposition of these or allied unstable compounds.

Electrochemical Action.—In the consideration of the reaction of iron with nitric acid the possibility is not to be overlooked that electrochemical action may occur between the constituents of samples which are not homogeneous. The electrochemical action which may take place will depend upon the potential differences of the surfaces exposed, and will also be affected by the concentration changes which arise from incomplete diffusion of the reagents in the liquid. The relationship of the potential to the action of nitric acid on iron is very obscure. Without venturing, at this stage, upon the discussion of a subject in which the data are as yet incomplete, it may be remarked that the absence of any pronounced difference in the reactions at 100° C. as between iron samples of the highest purity and uniformity obtainable and iron containing small particles of another constituent, such as cementite, is an indication that the reaction products of the iron are not essentially modified by the presence of foreign bodies. With regard to the effect of local concentrations in the electrolyte, it is evident that, so far as these represent a change in the concentration of the reacting NO_3 group, they will cause the corresponding change in the reaction products. Such concentrations will be prevented to a large degree by the violent stirring caused by the evolution of the gases, especially at temperatures near 100° C. For this reason alone it is certainly preferable to dissolve the sample at that temperature.

(4) *The Reaction-Curve.*

In the present investigation the results given by each sample are expressed by plotting the total iron-equivalents of the nitrogen and ammonia formed against the acid-strength used, and the curve so obtained has been termed the "reaction-curve" of the sample. The graphical method of presenting the results has been preferred on account of the difficulty of forming a correct idea of the changes in the reaction from a table of numerical results of analysis. The scale employed allows the points to be recorded with an accuracy within the limits of error of the analyses, and the presentation of the results in this way avoids the voluminous tables which would otherwise be required.

The use of a single curve has been rendered possible by the fact that nearly all the essential variations in the reactions are represented by changes in the total iron-equivalent of the ammonia and nitrogen. Four products have to be considered, namely, ammonia, nitrogen, nitric oxide, and nitrogen peroxide, but they are connected by certain special relations, so that the chief interest of the reaction centres in the above equivalent. The nitrogen and ammonia are connected by the relation that for a given sample and acid-strength the sum of their volumes is nearly constant although the irrelative amounts are liable to irregular variations. This has been shown to be due to the formation of nitrogen by the decomposition of ammonium nitrite in a secondary reaction (p. 20). How far the whole of the nitrogen evolved is so formed is uncertain, but it seems most likely that the main variations in its quantity arise from the secondary reaction. The interchange takes place according to equations, p. 22, and it will be seen that three volumes of ammonia and two of nitric oxide are required to form three volumes of nitrogen ; the iron-equivalent of this secondary nitrogen therefore includes that of the nitric oxide destroyed, which forms one-fifth of the total. Thus, owing to the presence of secondary nitrogen, the total iron-equivalent of the nitrogen and ammonia obtained is too high; if all the nitrogen were secondary its equivalent should be reduced by one-fifth, but this is probably not the case, and the true correction necessary to reduce the equivalent to that of the primary products will therefore be less than the above amount. Seeing that it is not possible to arrive at the true correction, the sum of the nitrogen and ammonia-equivalents has been taken as an approximate measure of the primary ammonia and nitrogen formed; by taking this total, a quantity is obtained which is nearly independent of the secondary transformation of ammonia to nitrogen.

A relation in many ways similar to that just mentioned exists between the nitric oxide and nitrogen peroxide, the iron consumed in producing the two gases remaining constant for the same sample and acid-strength while their proportions may vary (p. 24). Here, again, the formation of nitrogen peroxide may be regarded as a secondary transformation of a reaction product (possibly either nitrous acid or hydroxylamine) which normally gives rise to nitric oxide.

Thus the products of the reaction of iron with nitric acid fall into two groups, namely, (1) nitrogen and ammonia, (2) nitric oxide and nitrogen peroxide, the ratio between the iron-equivalents given by the two groups being approximately independent of the secondary reactions between the members within each group. A second characteristic of this grouping is shown in Fig. 3. Here, when the critical value is reached at which the ammonia suddenly gives place to nitric oxide, the nitrogen and ammonia decrease together, while the nitric oxide and nitrogen peroxide increase together; this is observed in the reactions of all iron and steel samples with nitric acid, and appears to indicate that the members of each group have something in common in their mode of formation. The "reaction-curve" which shows the boundary between the two groups is plotted from the values of the nitrogen and ammonia group, since the nitrogen peroxide is not estimated in the method of analysis used. It is clear, however, that practically the same curve could be obtained by suitably plotting the values of the nitric oxide and nitrogen peroxide group, in which the small amount of nitrous oxide formed should probably be included.

The two groups under consideration are each, in all probability, the result of a complicated series of changes. With further investigation the conception of the "primary reaction-product" may possibly be extended so as to include all the earlier and less stable configurations which first appear when the NO_3 molecule enters the field of reaction and precede the formation of reaction products such as ammonia, which have sufficient stability to be chemically identifiable. It is clear from the data already given that, with a given sample of iron, at some phase in these changes the concentration of the NO_3 group in the acid used exercises a determining influence upon the course of the reaction and is the deciding factor in the choice between two possible reaction-series which lead respectively to the ammonia-nitrogen group or to the nitric oxide-peroxide group. With a given concentration of NO_3, a similar determining influence is exercised by strain in the iron, and the investigation of the conditions governing these effects, as they are expressed in the reaction-curve, forms the subject of Part II. of this Report.

PART II.

The Effect of Strain upon the Reaction of Iron with Nitric Acid.

The method for the detection of strain which forms the subject of the present research is based upon the very remarkable changes in the reaction of iron with nitric acid which are brought about when the metal is cold-worked. This method is thus purely chemical in character, and depends upon the analysis of the reaction products by the method which has already been fully described in Part I.; the mechanism through which the physical condition of the metal influences the chemical reaction remains at present entirely unexplained.

The nature of the changes in analysis which take place is seen in Table VII., in which are given the results of some preliminary experiments made to ascertain the extent of the variations produced in a few typical cases by different methods of cold-working.

TABLE VII.—*Gases evolved from* 0·3-*gramme Samples dissolved at* 100° *C. in Acid-Strength* 33·5.

	Hammering.		Drilling.		Wire-drawing.	
	Normal.	Cold-worked.	Normal.	Cold-worked.	Normal.	Cold-worked.
NO	96·0 c.c.	50·0 c.c.	75·0 c.c.	55·0 c.c.	66·0 c.c.	46·0 c.c.
N_2O	1·0 ,,	2·0 ,,	2·0 ,,	4·0 ,,	3·5 ,,	2·0 ,,
N_2	3·0 ,,	5·0 ,,	6·0 ,,	4·6 ,,	7·0 ,,	7·0 ,,
NH_3	1·2 ,,	16·7 ,,	5·5 ,,	13·0 ,,	7·5 ,,	15·4 ,,
$Fe = (N_2 + NH_3)$	0·033 gm.	0·153 gm.	0·087 gm.	0·125 gm.	0.108 gm.	0·161 gm.
Fe = Total	0·280 ,,	0·291 ,,	0·288 ,,	0·290 ,,	0·296 ,,	0·289 ,,

The effect of the strain is well seen in the large variations produced in the iron-equivalent of the nitrogen and ammonia group. This effect offers a convenient means of detecting strain in such samples, and the investigation recorded in the present Report has shown that, with proper precautions, the method can be used in a great variety of cases for the comparison of the changes produced in samples of iron by varying mechanical and thermal treatments.

Since the iron-equivalent of the ammonia-nitrogen group has been raised as a result of cold-working, the position of the reaction-curve for the sample will have been altered. For the complete study of this effect it is therefore necessary to consider not merely the action with a single acid-strength, as given above, but the whole of the changes as expressed in the reaction curve. An example of the effect of cold-work on the reaction-curve of a sample of pure electrolytic iron (sample No. 1, Table XI.) is shown in Fig. 10; A is the curve given by the unstrained material, and B is that given by the drillings. The alteration due to cold-work is here very great; similar changes, though differing in degree, have so far been observed to result in every case from the mechanical deformation of iron and steel samples.

This method for the detection of strain offers several advantages over those which might be derived from the correlation of the degree of strain with the physical tests. The influence of cold-working on the physical properties of iron and steel has been much studied, but the form and size of the sample required in making tensile, bending, magnetic, and similar tests severely limits their application in cases where the sample is small and of irregular shape. A class of properties to which this objection does not apply includes the solution potential and some thermo-electric properties; these, while measurable in very irregularly shaped samples, depend entirely upon the state of the surface tested, and serious variations may arise from the cold-working of the surface which is inevitable in cutting and preparing the sample. If this superficial strained material is removed by chemical means, accumulation of the less soluble constituents may occur. Most important, however, is the uncertainty which affects the results when the sample is a mixture of two or more constituents; it is only necessary to refer to the literature describing the electrochemical behaviour of iron[1] in order to realise how great a mass of conflicting evidence has already accumulated on this subject.

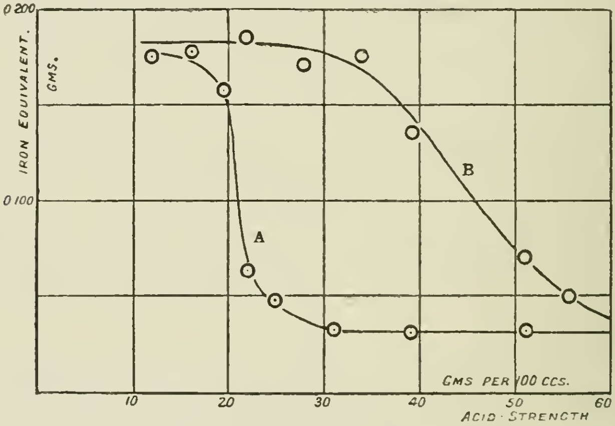

Fig. 10.—Electrolytic Iron: A. unstrained; B, drillings.

In the present case use is made of the average analysis of the gases evolved when the sample is dissolved in nitric acid; consequently slight local disturbances either at the surface or in the body of the metal do not unduly affect the result. The results are also entirely independent of the presence of flaws or inclusions and of the size and shape of the sample, while the amount required is sufficiently small to be obtainable in most cases which arise in practice. Most of the tests here recorded have been repeated at one time or another, and it was found throughout that, provided due care is exercised in the preparation of the samples, duplicate tests, whether made on the same day or at intervals of several months, agree very closely.

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[1] A number of references are compared by Cushman, "Corrosion of Iron and Steel," p. 83.

The physical changes brought about by cold-working, and the restoration of the properties by subsequent annealing, offer a wide field for investigation. In the following portion of this Report an account will be given of the changes produced in the reaction-curve of iron by two well-known methods of cold-working, namely, the twisting of wires and wire-drawing. For the interpretation of the results thus obtained it was found necessary to consider the behaviour of substances which are a mixture of two constituents, and examples will be discussed in some detail. An instance of the progressive removal of cold-work by annealing at increasing temperatures is next described, after which, in order to complete the evidence on this question, a careful test is made to ascertain whether grain-size has any influence on the form of the reaction-curve in the absence of other causes of variation.

(1) *The Effect of Successive Increments of Strain on the Position of the Reaction-Curve.*

The fact having been established that by straining a piece of iron its reaction with the various strengths of nitric acid can be completely altered, an endeavour was next made to ascertain the mode in which this change in the reaction-curve progresses with successive increments of strain. This investigation would have been much simplified if a means could have been found for producing in the specimens used deformations varying in amount, but in each case uniformly distributed. It is very doubtful, however, whether such uniformity is ever attainable in practice; apart from the fact that a cold-worked metal is essentially heterogeneous in structure, different portions of the mass nearly always suffer varying degrees of distortion when strained. In examining the effect of successive increments of strain, only samples which were really mixtures of strained material could therefore be employed.

Whatever method is adopted for producing strain, the first essential, in studying the effect on the reaction-curve, is to be able to obtain any number of samples of the same material equally cold-worked. The modes of deformation found to be most suitable for this purpose were, (1) drilling ; (2) wire-drawing ; (3) torsion of wires. The first was found to yield samples of great uniformity, but these were highly strained, and no intermediate stages could, of course, be obtained. In wire-drawing, successive drafts yield progressively strained samples, but no direct estimate of the work done in the process is available. By twisting lengths of wire it is possible to obtain samples having varying degrees of strain, and by measuring the torque to obtain a direct estimate of the total energy expended in producing the deformations. The changes produced through increasing deformations by the last two methods will now be described.

Reaction of Swedish Iron Wire deformed by Torsion.—The analysis of the material used in these experiments is given in Table XI. (sample 2). The diameter of the wire was 0·55 millimetre.

Preliminary Annealing.—It is evident htat, in order to obtain varying degrees of strain, all the samples used must first be reduced to a uniform condition, and any strain which may be present in them due to previous cold-working must be removed. The annealing of cold-worked iron has been studied by Goerens,[1] who found that strain effects are removed by heating the metal for a short time at about 550° C. In the experiments described below the lengths of pure iron wire to be twisted were, therefore, first heated for thirty minutes at this temperature. Later experiments on annealing have confirmed the view that this treatment suffices for the removal of almost all the effects of cold-work in pure iron.

Method of Twisting.—A piece of the annealed wire, about 7 inches long, was gripped at each end by two small clamps, the distance between which was such that the length of wire to be twisted had a weight of 0·300 gramme. One clamp was attached to a handle by which it could be revolved, a ratchet counter being provided to record the number of turns. The other clamp was attached to one end of a spiral spring which was kept slightly extended by the pull of the wire, the further end being fixed to a rigid support ; this spring served to take up the elongation of the wire which occurs in twisting, and also afforded a means of measuring the torque on the wire at any moment. For the latter purpose, a small pointer was attached to the end of the spring near the wire, and as the wire was twisted the pointer moved over a dial which was calibrated so as to indicate the moment of the couple acting on the end of the wire. As the wire was twisted, the pointer was more and more deflected until the yield point of the wire was reached, after which, on steady rotation of the handle, the deflection increased slowly, and at 250 turns had become almost twice that at which the permanent deformation began. Wires annealed at about 550° C. could usually withstand from 250 to 300 turns before breaking ; if the annealing temperature was raised, they broke earlier, owing, no doubt, to an increased grain-size. The curves in Fig. 11 show the relation between the torque and the number of turns given in three different tests ; from these curves the work done upon the wire can be calculated, being represented by the area between the curve and the horizontal axis. This figure indicates the total energy expended in twisting, and therefore includes both the energy stored in the wire through cold-working and the amount dissipated as sensible heat. No attempt has yet been made to ascertain the proportion of the latter, and it is not at present certain whether the amount of energy stored in the wires

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[1] *Iron and Steel Institute: Carnegie Scholarship Memoirs,* 1911, p. 320.

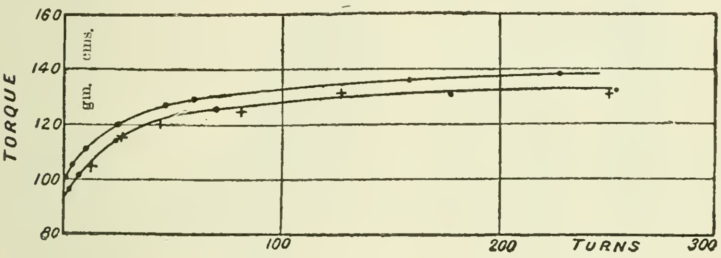

Fig. 11.

is even roughly proportional to the work done in twisting them. By this method of cold-working, however, any number of wires equally strained can be obtained.

The deformation which occurs in a wire twisted to the breaking point in this way is not uniformly distributed, the greatest strain being found in the outer portions, while the axial line is but little disturbed. Hence the results obtained on dissolving the whole wire after, say, 250 turns belong really to a mixture, the constituents of which have undergone varying amounts of deformation. The reaction-curves for the annealed wire and for the wire after twisting 5, 25, 50, 100, 150, 200, and 250 turns are plotted in Fig. 12. As in the case of drillings (Fig. 10) cold-working has caused the curve to be moved considerably towards the right, and this change takes place progressively as the work done on the wire is increased.

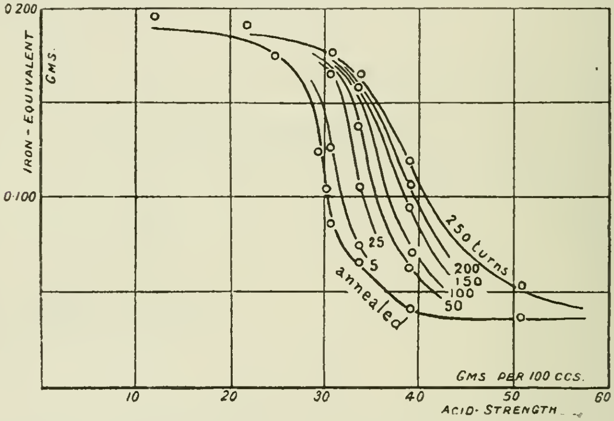

FIG. 12.—Reaction-Curves of twisted Iron Wires.

Another aspect of these results is presented in Figs. 13 to 16, in each of which the change of reaction brought about by increasing strain is plotted for a single strength of acid.

Sensitiveness of the Test.—From the graphs just given, it is evident that the change in analysis which is produced with a given acid by a small difference in the work put on the wire varies according to the acid-strength employed and the work already on the wire. To detect a certain small work-difference it will be best therefore to use that acid for which the corresponding part of the curve is steepest; for example, a work-difference of 10 turns between wires having about 150 turns is most easily detected by using acid-strength 39 (Fig. 13), while a difference of 5 turns in wires having about 25 turns can most suitably be shown by using acid-strength 33·5 or thereabouts (Fig. 14). The first few turns on an annealed wire can readily be detected by the changes in reaction with acid-strengths between 28 and 34, as is shown in Table VIII. It will be observed that, as the degree of strain is increased, the sensitiveness of the test, as judged by the comparison of differences produced by a small number of turns, diminishes.

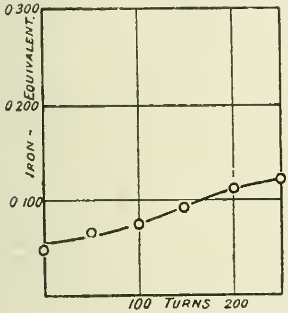

Fig. 13.—Acid-Strength, 39.

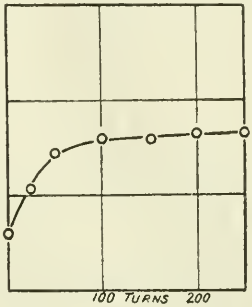

Fig. 14.—Acid-strength, 33½.

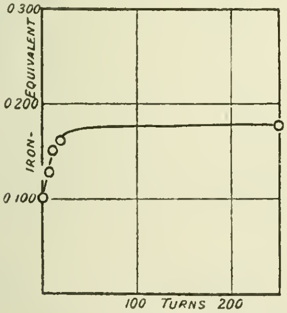

Fig. 15.—Acid-strength, 30½.

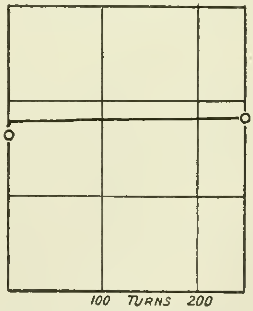

Fig. 16.—Acid-strength, 27½.

TABLE VIII.

Acid-Strength.	No. of Turns.	NO.	N_2O.	N_2.	NH_3.
29	0	72·0	2·0	4·0	10·1 c.c.
	5	61·0	2·0	3·5	13·9 ,,
	10	52·0	2·5	4·0	17·2 ,,
	15	50·0	2·5	4·5	18·0 ,,
33·5	0	86·0	1·5	2·2	6·4 ,,
	5	78·0	2·0	1·5	9·0 ,,
	25	67·0	2·0	3·0	12·0 ,,
	50	56·0	2·5	3·5	16·2 ,,

Thus the small deformation represented by about two turns on the annealed wire could readily be detected with acid-strength 29 through these changes in the analysis of the reaction products.

By means of the torque curve (Fig. 11) it can be calculated that the energy expended in giving 5 turns to the 0·3 gramme of annealed wire is approximately 3·0 × 10^6 ergs. The volume of 0·3 gramme of iron is about 0·037 cubic centimetre, and therefore the quantity of work detected in this case must be less than 80 × 10^6 ergs per cubic centimetre, since the energy actually absorbed is less than this by the heat produced during twisting. The average decrease in the volume of nitric oxide formed, due to the application of this small amount of work, is 11·0 cubic centimetres with acid-strength 29, and the iron-equivalent of the nitrogen and ammonia is raised from 0·10 to 0·12 gramme.

The sensitiveness of the test is well seen on calculating the rise in temperature which would occur if all the energy given to the wire in twisting were converted into heat. As already shown, the work done on 0·3 gramme of wire in making 5 turns is 3·0 × 10^6 ergs, which is equivalent to 0·072 calorie. Taking the specific heat of iron as 0·11, 0·072 calorie would raise the temperature of the sample about 2° C. As an energy difference represented by only two turns can be detected, it may therefore be concluded that the method will detect in annealed iron the absorption of energy which, if converted into heat, would not be sufficient to raise the temperature 1·0° C.

Reaction of Soft Steel Rod deformed by Wire-drawing.—In investigating the effect of cold-working on the physical properties of metals much use has been made of deformation by wire-drawing. Unlike that produced by twisting, this deformation is fairly uniformly distributed across the section ; it is also uniform throughout the length of the wire, so that any number of equally strained samples may be obtained. The amount of work done in drawing is not, however, so easily measurable as in the case of wire-twisting. Goerens [1] takes the " percentage reduction of area " as a measure of the deformation and finds this to be proportional to the maximum stress.

For the present experiments a set of wires of different gauges was drawn from a sample of soft steel rod (sample 5, Table XI.). Their diameters are given in the second column of the following table :

Table IX.—*Results obtained from Drawn Wires.*

Treatment.	Diameter.	Percentage Reduction of Area.	$Fe = N_2 + NH_3$. (Acid-strength 39)	Middle Point of Curve.
	Centimetre.		Gramme.	
Untreated	0·52	0	0·056	34·0
1st drawing	0·40	41	0·107	40·5
2nd ,,	0·31	64·5	0·123	44·0
3rd ,,	0·265	74·0	0·133	45·5
4th ,,	0·194	86·0	0·137	46·0
5th ,,	0·163	90·0	0·142	46·0

The complete reaction-curves for these samples are plotted in Fig. 17 (p. 38). The progressive shift of the curve to the right with successive increments of strain is again seen.

The similarity between this set of curves and that given by the twisted wires (Fig. 12) is very marked, but it will be observed that the curves for the latter are somewhat steeper.

In Fig. 18 (p. 39) the change in the iron-equivalent of the nitrogen and ammonia given by the drawn wires is plotted against the percentage reduction of area, and it will be noticed that about the fourth drawing this value tends to become constant. Since the effect of cold-working is to cause a displacement of the curve, this result would seem to indicate that the energy content of the iron is but little altered by the final drawings. On the other hand,

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[1] *Loc. cit.*

Goerens found that the tensile strength increased proportionally even up to 90 per cent. reduction of area. The discrepancy is small, however, and need not be further discussed here, for the tensile test result does not necessarily depend solely upon the energy-content, as it is well known to be influenced by grain-size and other purely structural conditions.

(2.) *Theoretical Considerations involved.*

Before the interpretation of the results given by the various samples examined can be attempted, it will be necessary to consider, (1) the form of the reaction-curve which should be obtained when a sample consisting of a mixture of two or more constituents, each with a characteristic curve, is treated according to the method, and (2) the extent to which this form may be modified by electrochemical action in dissolving.

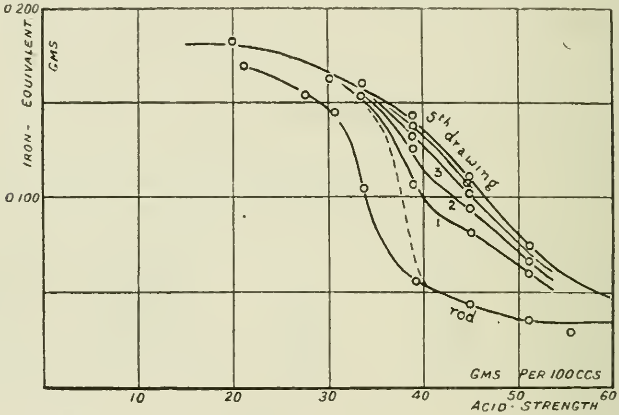

Fig. 17.—Reaction-Curves of Drawn Wires.

(1) *The Mixture-Rule.*—If two constituents, in the form of fine particles, are mixed together and dissolved, it is evident that the reaction of each particle will proceed uninfluenced by the others, provided that the reaction is fairly rapid so that the liquid is well stirred to prevent local concentrations. The quantities of the gases evolved from 0·3 gramme of such a mixture would

then be equal to the sum of those given by the weights of the two constituents used. Each point on the reaction-curve obtained will therefore be determined by the values for the same acid-strength on the reaction-curves of the constituents. If, with a given acid-strength, the value for the constituent A is x, and for B is y, then the value for a mixture of $mA + nB$ ($m + n = 0\cdot3$ gramme) is :

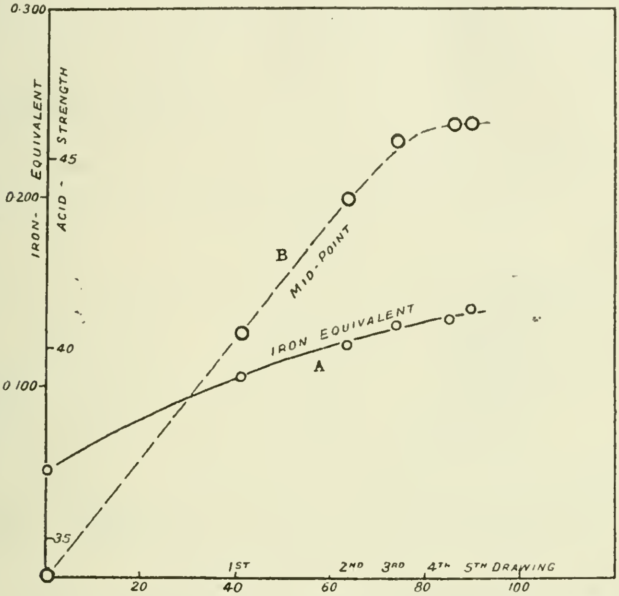

FIG. 18.—Drawn Wires : A, iron-equivalents of ammonia + nitrogen formed with acid-strength 39 ; B, acid-strength corresponding with the mid-point of the reaction curve ; plotted against the percentage reduction of area.

$$\frac{mx + ny}{0\cdot3} = x + \frac{n}{0\cdot3}(y - x).$$

Thus the new reaction-curve can be found by dividing the vertical distance between the curves of the constituents in the ratio $n : m$. In general, for mixtures whose constituents yield values x, y, z, &c., the final co-ordinate X is :

$$x + \frac{n}{0\cdot3}(y - x) + \frac{p}{0\cdot3}(z - x), \text{ \&c.}$$

In Figs. 19 and 20 examples are given of the curves resulting from the combination of outer reaction-curves A and B, which are types commonly found ; the intermediate curves are those given by the mixture-rule for the compositions indicated.

(2) *Deviations due to Electrochemical Action.*—When the constituents of the mixtures exist, not as separated particles, but in close metallic contact, as is the case with iron and steel samples, it is not permissible to assume that the reaction accompanying the solution of any particle is uninfluenced by electrochemical action which may occur between that particle and a neighbouring constituent. Before the mixture-rule can be safely applied in interpreting the various curves obtained, it is essential that the degree to which electrochemical action may have caused deviations from the true mixture-curve should be at least approximately ascertained. It is possible, by testing known mixtures, to arrive at an estimate of the deviations which may occur, and to find the conditions under which such deviations are reduced to a minimum.

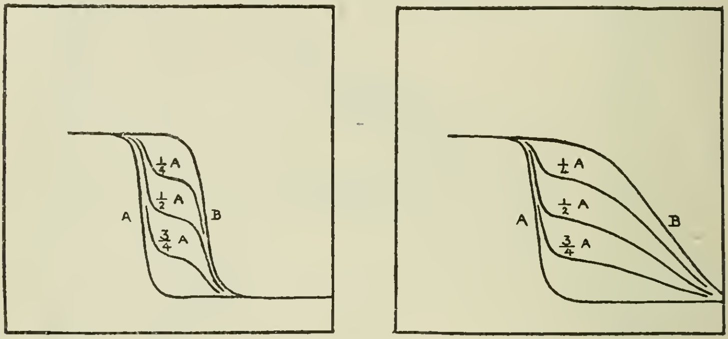

Fig. 19. Fig. 20.

Types of Reaction-Curve required by the Mixture-Rule for mixtures of two constituents having the curves A and B.

In studying this question two courses are available. In the first place, means may be taken to vary the degree of electrochemical action as, for example, by dissolving at a lower temperature than 100° C. Two instances of the differences obtained in this way, when using approximately homogeneous material, have already been given (p. 17), and it was shown that, even with the purest iron, there was a small but unmistakable movement of the reaction-curve to the right at the lower temperature; this movement was, however, partially due to secondary reactions. On general grounds there is reason to expect a certain movement of the curve, and this change may be regarded as a definite temperature effect characteristic of all samples of pure iron and not necessarily electrochemical in nature. Special electrochemical action due to the presence of another constituent will therefore appear, when dissolving at lower temperatures, as a deviation from this normal change.

A second course which may be employed to ascertain the extent to which the mixture-rule can be applied lies in the comparison of the curves given by known mixtures with the theoretical curves calculated by the mixture-rule. This direct way is the more satisfactory of the two, but unfortunately its use is very restricted, as it is not easy to obtain mixtures for which the reaction-curves of the constituents are known with certainty. The curves must nearly always be taken as those given by independent preparations of constituents which are considered to be identical with those present in the mixture used. In dealing with iron and steel samples, the two most suitable mixtures so far obtained are (*a*) ferrite and cementite and (*b*) ferrite and martensite; the reactions of these will next be described.

(*a*) *Reaction-Curves for Mixtures of Ferrite and Cementite.*—The sample used was a wire-drawing plate (sample 6, Table XI.) which had been thoroughly annealed, so that the pearlite originally present was in a completely divorced condition, as shown in Photo 1. There can be little doubt, therefore, that in this case the reaction-curve of the ferrite in the unstrained sample is closely similar to that shown in Fig. 3. Before describing the experiments with this mixture, it will be necessary to consider the form of the cementite curve, and in view of the importance of cementite in the carbon steels, it will be as well at this stage to discuss its reaction with nitric acid in some detail.

Reaction Curve of Cementite.—Cementite contains 93·33 per cent. of iron and 6·67 per cent. of carbon; 0·3 gramme will therefore contain 0·02 gramme of carbon, and on dissolving in nitric acid the quantities of reduction products formed will be equivalent to those given by 0·28 gramme of iron together with those due to the solution of the carbon. The reaction of the carbon takes place in two stages; first one or more hydrocarbon compounds are formed, and these are then slowly oxidised to carbon dioxide by the acid, with the evolution of the usual reduction products. If the whole of the carbon present were oxidised to carbon dioxide the volume of the reduction products would be 6·2 times the volume which could be obtained from the same weight of iron,[1] so that in this case the apparent iron-equivalent of the gases obtained from 0·3 gramme of cementite would be $0{\cdot}28 + 0{\cdot}02 \times 6{\cdot}2 = 0{\cdot}404$ gramme. A complete oxidation of the carbon is never attained in practice; even with 39 acid-strength only about 20 per cent. is evolved as carbon dioxide in the first ten minutes' boiling, and the rest is either liberated as hydrocyanic acid or remains in the solution in an intermediate state of oxidation.[2]

The composition of the complex hydrocarbons very frequently approximates to that represented by the formula (CH_2). This may, therefore, be taken as an example in illustrating the effect produced on the total iron-equivalent of the gases evolved from cementite when a hydrocarbon is formed. The formation of a hydrocarbon not only prevents the carbon from reducing nitric acid, but also sets free an amount of oxygen equivalent to the hydrogen used. The reaction is thus oxidising in character, and will therefore partially counteract the reducing action of the iron, as will be seen from the following equations in which nitrogen peroxide has been taken as the final product:

$$\begin{aligned} C + HNO_3 &= CH_2 + 2NO_3 \\ 2NO_3 + 2NO &= 4NO_2. \end{aligned}$$

In this instance, owing to the formation of the hydrocarbon CH_2, two molecules of nitric oxide (or an equivalent amount of some other reduction product present in the solution, *e.g.* $6NO_2$) are replaced by four molecules of nitrogen peroxide. Consequently

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[1] The equations concerned are as follows;

$$\begin{aligned} &(1)\ C + 4HNO_3 &&= CO_2 + 2H_2O + 4NO_2. \\ &(2)\ 3C + 4HNO_3 &&= 3CO_2 + 2H_2O + 4NO. \\ &(3)\ 2C + 2HNO_3 &&= 2CO_2 + H_2O + N_2O. \\ &(4)\ 5C + 4HNO_3 &&= 5CO_2 + 2H_2O + 2N_2. \\ &(5)\ 2C + H_2O + HNO_3 &&= 2CO_2 + NH_3. \end{aligned}$$

According to these equations 1 gramme of carbon would yield either (NO_2) 7430 c.c., (NO) 2475 c.c., (N_2O) 930 c.c., (N_2) 744 c.c., or (NH_3) 930 c.c. These volumes are 6·2 times those given by 1 gramme of iron (p. 3).

[2] J. H. Whiteley, *Carnegie Scholarship Memoirs*, vol. viii. p. 12.

for every gramme of carbon transformed to the hydrocarbon the iron-equivalent of the gases evolved from the iron of the cementite will be reduced by an amount equal to 3·1 grammes of iron while no reduction products are yielded by the carbon. Thus, when using 0·3 gramme of cementite, if all the carbon were transformed to CH_2, the total iron-equivalent of the gases liberated would only be $0{\cdot}3 - 0{\cdot}02 - 0{\cdot}02 \times 3{\cdot}1 = 0{\cdot}218$ gramme; on subsequent oxidation of the hydrocarbon through continued boiling the iron-equivalent of the gases would be gradually raised, owing to the further evolution of oxides of nitrogen, until the highest possible value—0·404 gramme—had been reached. In actual practice it is found that the two actions proceed simultaneously, so that the iron-equivalent remains fairly constant in the first few minutes' boiling and then gradually rises, especially when using the stronger acids. An instance of the increase in iron-equivalent obtained by continued heating of the solution is given below. Two portions of the wire-drawing plate (c.c. 2·35 per cent.), which contains 35 per cent. of cementite, were tested in the usual way; in one case the solution was boiled for one minute, and in the other for twenty minutes.

Acid-Strength.	Boiled.	NO.	N_2O.	N_2.	NH_3.	Fe-equiv.
33·5	1 min.	67·5 c.c.	3·0 c.c.	4·5 c.c.	8·3 c.c.	0·282 gm.
33·5	20 ,,	69·5 ,,	3·0 ,,	10·5 ,,	4·2 ,,	0·309 ,,

In order to obtain the reaction-curve of cementite, a quantity of this substance was prepared from a bar cut from the wire-drawing plate; the method of preparation used was that described by Arnold and Ibbotson.[1] Portions weighing 0·30 gramme were dissolved in the various acid-strengths, and each test was boiled for about five minutes, so as to ensure complete solution of the cementite. The analyses of the gases liberated are given in Table X. (p. 44). (CO_2 is not included.)

Here again, for the reason given above, the total iron-equivalents are high in some cases; with acid-strength 45 this increase is not seen owing to the formation of larger quantities of nitrogen peroxide. The reaction-curve for cementite obtained by plotting these results is shown in Fig. 21, curve A, and it will be noticed that it has the same general form as the curve for pure iron, but the change in the reaction is not so abrupt.

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[1] "Steel Works Analysis," p. 436.

The reactions of cementite having been discussed, the experiments which were made with the ferrite-cementite mixture (p. 41) can now be described. The reaction-curve given by drillings of this sample was first obtained by dissolving 0·30 gramme portions at 100° C. and boiling for about five minutes. The curve is plotted in Fig. 21 (curve B); it is almost a straight line, and lies between the curve for strained ferrite,[2] shown by the broken line C, and that for cementite A. According to the analysis, the material contains 35 per cent. of cementite and 65 per cent. of ferrite; if the cementite curve A and strained ferrite curve C are combined in this proportion by the mixture-rule, the resultant curve is that shown at D. This is closely similar in shape to the curve actually obtained, though situated somewhat above it, and it is clear that in this instance the mixture-rule is approximately obeyed.

TABLE X.—*Volumes of Gases evolved on Dissolving* 0·3 *gramme* Fe_3C *in Nitric Acid.*

Acid-Strength.	11·5.[1]	16·5.	21·5.	27·5.	33·5.	45·0.
NO	53·0	67·0	81·0	92·0	94·0	88·5 c.c.
N_2O	7·0	6·0	5·0	4·0	5·0	5·0 ,,
N_2	7·8	7·0	6·0	6·7	4·5	3·7 ,,
NH_3	9·8	5·1	3·6	1·6	1·8	0·2 ,,
Fe total	0·309	0·300	0·309	0·324	0·317	0·286 gm.
$Fe = N_2 + NH_3$	0·130	0·092	0·074	0·067	0·049	0·032 ,,

Portions of the same drillings were next dissolved at 60° C. and the tests afterwards boiled for five minutes. These tests yielded more nitrogen and less ammonia, small corrections (p. 27) were therefore required in order to make the results strictly comparable with those above. The figures obtained are plotted in the curve E. There is no doubt that while the values about acid-strength 30 are those which would be expected after allowing for a small temperature-shift (p. 41), there is in addition an increased steepness with the higher acids. The mixture-rule still partially holds good in this case even on dissolving at 60° C. These experiments on a mixture of cementite and strained ferrite offer very strong evidence, therefore, that with such samples at 100° C. only a small degree of disturbance of the reaction occurs owing to metallic contact between the constituents.

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[1] Boiled fifteen minutes.

[2] The experiments which have so far been made indicate that the ferrite in high carbon steel drillings is not so highly strained as in pure iron drillings. The curve given here is that for a partially strained ferrite.

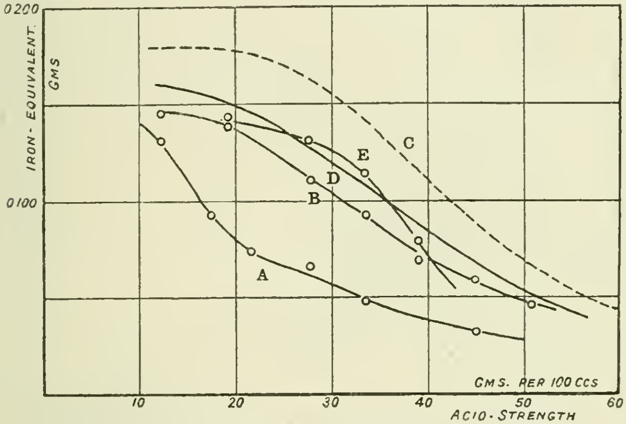

FIG. 21.—A. Reaction-curve of cementite.
B. ,, 2·5 per cent. carbon steel drillings.
C. ,, strained ferrite.
D. ,, mixture of $\frac{1}{3}$ A + $\frac{2}{3}$ C.
E. ,, 2·35 per cent. carbon steel drillings, at 60° C.

The reaction-curve was next obtained for cut (unstrained) pieces of the same sample. This curve is plotted in B, Fig. 22. The pieces were very slow in dissolving, especially with the weaker acids, from one to two hours being required in each case. The curves for unstrained ferrite C and for cementite A combined in the correct proportion yield a theoretical curve D, which is evidently close to that obtained with the higher acids, but which deviates to a marked degree about acid-strength 20. At this point there is, therefore, considerable evidence of electrochemical action; this is not surprising in view of the very slow solution of the samples, which, it may be remarked, was far slower than that for any of the ordinary steels or for iron.

(*b*) *Reaction-Curve for a Mixture of Ferrite and Martensite.*—The sample used was cut from a mild steel ingot (sample 4, Table XI.). The curve for this material in the pearlitic condition, as cast, in which it contained about 20 per cent. of pearlite, is shown in Fig. 23 (curve A). The broken line may be taken as the curve for the ferrite in this sample, the small deviation between this and curve A at about 33 acid-strength being due to the presence of pearlite. On comparison with the curve in Fig. 3, it will be seen that the ferrite curve in this steel is very similar to the curve given by pure iron.

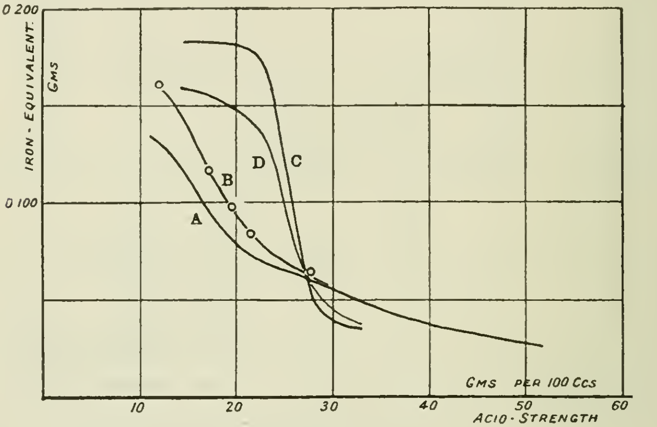

Fig. 22.—A. Reaction-curve of cementite.
B. ,, 2·35 per cent. steel unstrained.
C. ,, ferrite unstrained.
D. ,, mixture of $\frac{1}{3}$ A + $\frac{2}{3}$ C.

A small section was heated to 900° C., cooled slowly to 710° C., and then rapidly quenched. The structure obtained is shown in Photo 2, and consisted of a mixture of about 75 per cent. ferrite and 25 per cent. martensite. The martensite areas must therefore contain at least 0·6 per cent. of carbon. Here, again, the exact curve for this martensite is difficult to ascertain, for the Eggertz test indicates that in such a sample the parts containing the carbon are not in a fully quenched condition.[1] The curve given by this quenched sample is shown in Fig. 23 (curve B); that for a fully quenched steel containing 0·6 per cent. of carbon is given at C, but for the reason mentioned the martensite curve in the present instance should most probably be taken as the broken line D, representing an imperfectly quenched steel.

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[1] *Iron and Steel Institute: Carnegie Scholarship Memoirs*, vol. viii. p. 86.

The curve calculated for this sample from curves D and A by the mixture-rule is that shown at E, and lies near the experimental curve except at the higher acid-strengths. This slight fall of the experimental curve with the stronger acids is often observed when the constituent with the more advanced curve is present in comparatively small amount.

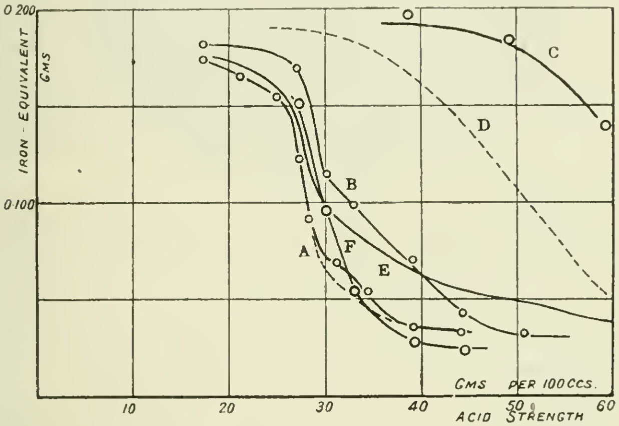

FIG. 23.—A. Reaction-curve of mild steel ingot.
B. ,, ,, ,, quenched from 750° C.
C. ,, 0·50 c.c. steel fully quenched.
D. ,, steel incompletely quenched.
E. ,, mixture of $\frac{1}{4}$ A + $\frac{3}{4}$ D.
F. ,, ingot quenched from 750° C., at 60° C.

When the sample was dissolved at 50° to 60° C., instead of 100° C., the reaction-curve obtained was that shown at F. The small depression with the higher acids already observed in the present instance when dissolving at 100° C. and in the case of the wire-plate dissolved at 60° C. is here greatly accentuated, and there can be no doubt that a very considerable increase in electrochemical action has been caused by dissolving this ferrite martensite mixture at the lower temperature; at 100° C., however, the mixture-rule still approximately holds good.

General Application of the Mixture-Rule.—From the behaviour of the two samples in the experiments just described, it may be concluded that the deviations from the mixture-rule of the results given by iron and steel samples are small at 100° C. ; a definite effect due to the metallic contact of the constituents is certainly present, especially when the rate of solution of the sample is slow, but this is not sufficient to cause serious error in the interpretation of the results. The mixture-rule may therefore be applied to reaction-curves obtained by dissolving at 100° C. samples the constituent particles of which are of similar dimensions to those shown in the photos. The experiments also show that an indication of the amount of deviation occurring at 100° C. can be obtained by dissolving a set of tests at a lower temperature ; owing to the slower rate of solution, electrochemical effects are thereby accentuated.[1]

The question at once arises whether finer-grained structures will not suffer a greater degree of electrochemical action and so yield results deviating seriously from the mixture-rule even at 100° C. The practical difficulties in the preparation of mixtures the constituents of which are in a finely divided state and have known reaction-curves are even greater than in the case of coarse-grained aggregates. It will be better, therefore, to consider this question when the reactions of such mixtures are examined, but it may be said here that the results of all the experiments so far made seem consistent with the view that the mixture-rule can still be applied in such cases.

Temperature Effect in Dissolving the Twisted Wires (p. 32).—One instance of a fine-grained mixture has already been given ; the twisted wires are almost certainly mixtures of more and less highly strained material, and before discussing the conclusion to be drawn from the experiments made with these wires it is necessary to ascertain the extent to which the results at 100° C. may be affected by electrochemical action. For this purpose the reaction-curve was determined for wires twisted 250 times and

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[1] The evidence given in a Report on the Eggertz test by one of the authors (*loc. cit.*) indicates that the carbon colour-value is affected by electrochemical action in dissolving. It is very difficult to arrive at an estimate of the amount of current sufficient to cause such variations, and it is not, at present, possible to say to what extent a deviation from the mixture-rule will be accompanied by a change in the colour-value of the carbon. All the evidence so far obtained suggests that the reaction of iron carbide with nitric acid is extremely sensitive, and that very small changes in current strength may suffice to cause variations in the amounts of coloured products formed.

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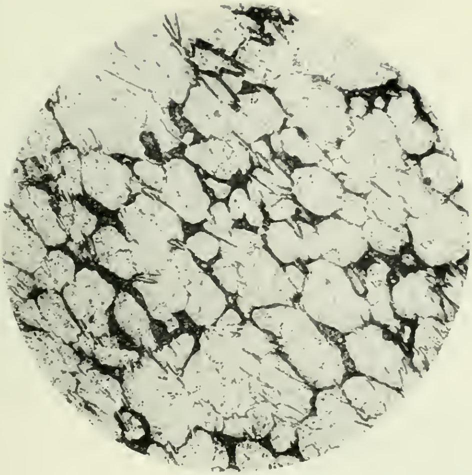
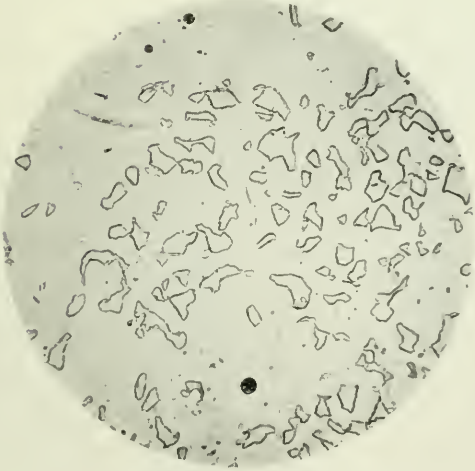


No. 1.—Steel, 2·35% carbon, annealed.
Stained with sodium picrate.

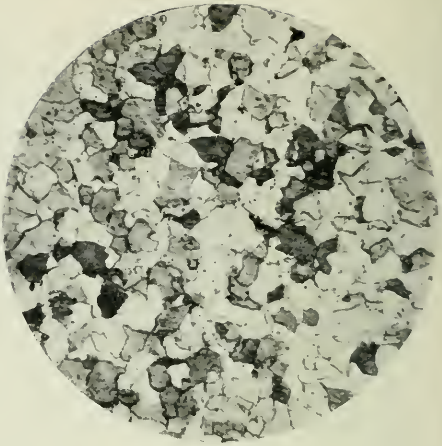
×135.



No. 2.—Steel, 0·15% carbon, quenched.
Etched with picric acid.

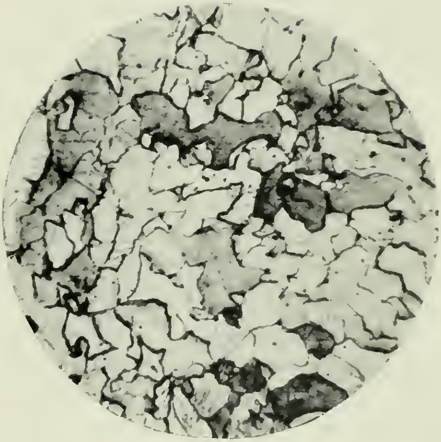
×135.

[*To face p.* 48.



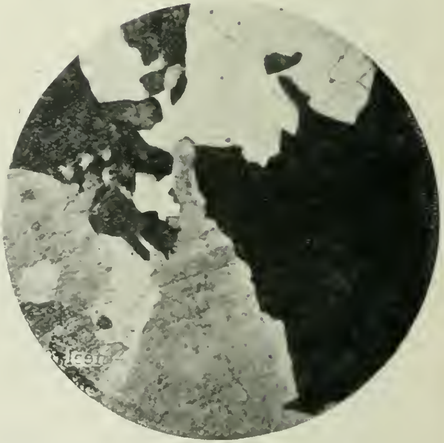
No. 3. × 63.

1 hr. at 1000° C.



No. 4. × 63.

1 hr. at 1250° C. and cooled,
then 5 mins. at 1000° C.



No. 5. × 63.

1 hr. at 1250° C.

"American washed iron" reheated to give various grain-sizes.

dissolved at 45° C., and is given in Fig. 24, together with that obtained at 100° C. The usual shift to the right of the 45° C. curve, due to true temperature effect, is again seen, and the curve is slightly steeper than the 100° C. curve. These experiments thus indicate that in dissolving at 100° C. no appreciable electrochemical action occurs between the differently strained parts of the material, and it is therefore permissible to apply the mixture-rule in discussing the results given by twisted and also by drawn wires.

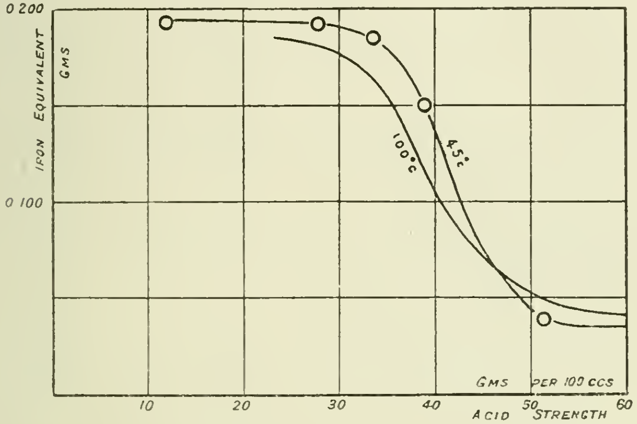


Fig. 24.—Reaction-Curves of Iron Wire twisted 250 turns; dissolved at 100° C. and at 45° C.

(3) *Relation between the Displacement of the Reaction-Curve and the Physical Changes in Strained Iron.*

An explanation, now generally accepted, of the effect of cold-working on the physical properties of metals is that "amorphous" material is produced in increasing quantity as the strain increases, the hardening and embrittling of the metal which usually takes place being the result of the presence of this "amorphous" form. In the view of some workers, the "amorphous" material, although non-crystalline, is sufficiently fixed in properties to justify the application to it of the term "amorphous phase." Thus Rosenhain defines it as follows: "Amorphous metal is therefore to be regarded as being identical in nature with the liquid metal if that could be cooled down to the ordinary temperature without undergoing crystallisation."[1]

According to this view, the properties of strained iron are those of a mixture of two distinct constituents, namely, crystalline *α*-ferrite and the amorphous phase, the distinguishing feature of the "phase" theory being that there is a discontinuity of properties between the two states. This explanation of the constitution of strained iron would require that the reaction-curve of such a sample should be that given by a mixture of these constituents. On reference to the curves in Figs. 12 and 17, it will be seen that the intermediate curves do not fulfil this requirement in its simplest form. The first effect of the admixture of a small amount of amorphous material would be to raise the lower part of the unstrained ferrite curve in the manner shown in curve $\frac{3}{4}$ A, Fig. 19, while the upper part would be very little affected. The form of curve actually obtained is well seen in the curves for the wires which were twisted 25 and 50 times (Fig. 12), and is rather the reverse of this ; the curve advances to an equal extent from top to bottom, so that its form is not altered. This implies that the state of the whole of the iron has been changed uniformly and not by admixture of a second "phase."

This lateral displacement of the curve progresses with increasing amounts of work until, in the case of the twisted wires, further striniang is prevented by the breaking of the sample. Up to this point little evidence of the existence of any second constituent of distinct character is to be seen, for the curves remain fairly steep and retain the simple form. With the drawn wires, fortunately, a much higher degree of cold-working is attainable. At the first drawing the curve has already been displaced to the position of that for a wire twisted 200 turns. Here, however, the lower portion of the curve shows very definite evidence of the admixture of some other constituent ; this and the remaining curves can be represented as mixtures of an iron having a displaced curve such as that shown by the broken line in Fig. 17, with an iron having the last curve of the series (5th drawing). The theoretical form of such curves is shown in Fig. 20.

The effect of straining these samples can be divided, then, into two distinct stages, in the first of which the curve is moved to the right, while in the second the form is modified in the manner required by the mixture-rule in the presence of a second constituent.

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[1] *Intro. Phys. Met.*, p. 249.

The explanation of the initial uniform alteration of the iron is probably to be found in the fact that before the crystal structure is destroyed, work must be done on the crystals in deforming them up to their elastic limit, and so the whole of the metal first becomes charged with a certain amount of energy, the crystals being at this stage in a condition resembling that of a mass of interlocking bent springs. The curve given by the iron in this condition will as a consequence be in advance of that given by the unstrained material. With increasing deformation the crystal structure begins to be progressively destroyed, and so from this stage onwards the metal will consist of a mixture of elastically strained crystals with an increasing amount of iron in which the crystal structure has been replaced to an indefinite extent by haphazard arrangements of the atoms; to the latter the term "amorphous" material may suitably be applied. A mixture curve is here to be expected, and is indeed observed. If all the iron crystals could be brought at once into the elastically strained condition without any destruction of crystal form occurring, the new position of the curve would most probably be about that shown by the broken line in Fig. 17. In practice the two stages must certainly overlap to an extent which may perhaps depend upon the method of cold-working.

It is remarkable that the curve for the wire after five drawings (Fig. 17), by which the area was reduced 90 per cent., is very close to that given by drillings of similar material; in no instance has any higher curve so far been obtained by any other method of cold-working. It would seem, therefore, that this curve corresponds nearly to the limit of strain by cold-working which iron will withstand.

It is generally considered that at this point the crystal structure has been to a large extent replaced by the amorphous condition; the curve will therefore be approximately the reaction-curve of the amorphous material. As might be expected, the form is not that of a crystalline phase such as is represented by the almost discontinuous curve for pure iron, but is that which can be derived from the mixture of a succession of simple curves.

The present experiments thus indicate that, while the first effect of cold-work is to carry the majority of the iron crystals to their elastic limit, with further deformation the crystal units become interlocked and remain in the elastically strained condition even when the stress is removed ; with still further deformation, these strained elements are converted progressively into amorphous material.

(4) *The Removal of Cold-Work by Annealing.*

The chemical method for the detection of strain can be employed in examining the progressive removal of strain due to cold-working on annealing at increasing temperatures. For this purpose the Swedish iron wire previously used was again taken ; a series of pieces, each twisted 250 turns, were annealed *in vacuo* at different temperatures up to 600° C. for a period, in each case, of thirty minutes. This period of time was selected because a number of tests in which the strained wires were heated for either one-quarter, one-half, or two hours at 400° C. all gave the same result by the method. These results are completely in accordance with the observations of Goerens, who found that at temperatures below 500° C. the amount of annealing which takes place is nearly all completed in the first fifteen minutes, after which time the properties of the sample remain fairly constant. In this respect the behaviour of a strained iron strongly resembles that of a quenched steel when tempered.

The wires after annealing at the various temperatures were now tested by the method. All the samples were dissolved in acid-strength 39 ; this acid was chosen because it yields a fairly uniform variation in the analysis with an increasing amount of strain, as will be seen on reference to Fig. 13. The change in the gas analysis which occurred as the annealing temperature was raised is shown in Fig. 25, where the temperature of annealing is plotted as abscissa and the number of cubic centimetres of nitric oxide evolved from 0·3 gramme of sample as ordinate. This quantity has been plotted in preference to the ammonia-nitrogen equivalent usually taken because of its greater sensitiveness in cases where the experiments are all made with the same acid under strictly comparable conditions.

The curve thus obtained indicates very clearly the increase in the degree of annealing which occurs as the temperature is raised. After annealing at 520° C. the analysis of the evolved gases is the same as that obtained on dissolving the original annealed wire, and remains nearly constant for temperatures up to 700° C. With acid-strength 39 the amount of nitric oxide here formed is nearly the maximum ever found with this acid, and so it is possible that the constancy obtained might be due to lack of sensitiveness of the acid in the later stages of annealing. A similar series of results was therefore obtained with acid-strength 33·5, which is much more sensitive to small differences in the later stages of annealing (p. 35). These results are plotted in the lower curve, Fig. 25, and it will be seen that the results given in the upper curve are completely confirmed. It is quite clear, then, that in the present instance the removal of the strain due to cold-working progresses with the greatest rapidity as the temperature of annealing approaches 500° C. and ceases when the temperature exceeds about 520° C., the sample having then returned approximately to its original state. These conclusions are entirely in accordance with those arrived at by Goerens when working with similar samples. It should be stated, however, that prolonged heating at temperatures well above 520° C. does cause a slight further change in the analysis, but it is evident that another effect is here concerned, entirely different from that due to strain, which is so completely removed at 520° C.

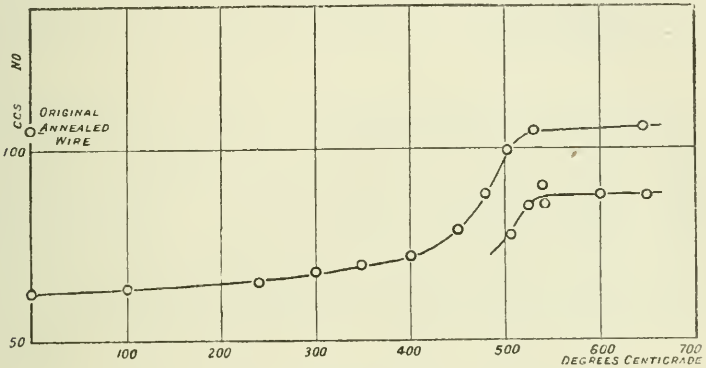

FIG. 25.—Nitric Oxide evolved from Twisted Iron Wires annealed at various Temperatures

In a paper on the "hardness and hardening" of metals by Turner[1] reference has been made to an observation first made by Howe, that cold-work effects are easier to remove from more highly strained pieces than from those having a lesser degree of strain. In the course of the present investigation an interesting corroboration of this statement was obtained. The following table shows the differences which were obtained on annealing two samples at 520° C.:

	NO.	N_2O.	N_2.	NH_3.	Fe.
Original wire annealed at 520° C.	77·0	2·5	3·5	9·0 c.c.	0·298 gm.
Do. twisted 250 turns, annealed again at 520 ° C.	83·0	2·0	3·0	7·3 ,,	0·295 ,,

It is clear that the annealing of the twisted wire has proceeded further than that of the annealed wire. Only by annealing the original wire at the higher temperature of 550° C. could the greater amount of NO be obtained from it. The small amount of strain which was present in the original wire, therefore, required a higher temperature to remove it completely than that necessary to remove the large amount in the heavily twisted wire.

Influence of Grain-Size upon the Reaction-Curve of Pure Iron.

Several physical tests are influenced in a high degree by the grain-size of the samples used, and it is not permissible to assume that the present test will be independent of this property unless definite evidence is available in support of such a conclusion. The theory has been advanced that the space between adjoining grains is occupied by an "intergranular cement" resembling the amorphous phase developed in cold-working; the thickness attributed to this layer is not always clearly defined, but since the cohesive properties are regarded as being modified by its presence, the thickness must be taken as commensurable with the dimensions of the grains themselves. Other workers have postulated considerably thinner layers, of "molecular" dimensions. Whatever view be adopted as to the molecular arrangements concerned, since the intercrystalline surfaces may, in general, possess surface energy the energy present in the sample should vary with the grain-size.

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[1] *Journal of the Institute of Metals,* 1917.

It has been shown that the chemical test now under discussion affords a means of detecting very small variations in the energy-content of samples of pure iron. It is therefore of considerable interest to sacertain by direct experiment whether any systematic difference can be observed between samples of the same material having varying grain-sizes. For this purpose three pieces of the pure "American washed iron" (sample 3, Table XI.) were given respectively the following heat-treatments, the rate of cooling being slow and about the same in each case:

TABLE XI.—*Analyses of Samples used in the Experiments.*

No.	Description of Sample.	C.C.	Si.	P.	S.	Mn.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	Electrolytic sheet iron . .	trace	0·015	trace	trace	0·01
2	Swedish iron wire, diam. 0·55 mm.	0·01	0·02	0·04	0·007	0·02
3	American washed iron . .	0·03	0·01	0·015	0·022	0·14
4	Acid steel ingot (section) . .	0·15	0·02	0·068	0·065	0·49
5	Basic steel wire . . .	0·07	0·008	0·084	0·056	0·67
6	Wire-drawing plate . . .	2·35	0·17	0·022	0·024	0·61

No. 1.—Annealed one hour at 1000° C.

No. 2.—Heated at 1250° C. for one hour, then cooled and reheated five minutes at 1000° C.

No. 3.—Heated at 1250° C. for one hour.

The very marked differences in grain-size thus produced are shown in Photos 3, 4, and 5. The number of grains in one cubic centimetre in each case was found to be as follows: No. 1, 27,000; No. 2, 4,000,000; No. 3, 15,000,000.

The reaction-curves for the three samples were now determined on carefully cut pieces, and are given in Figs. 26, 27, and 28.

The three curves are in the closest agreement throughout their length, and there can be no doubt that the reaction-curves of the three pieces are the same within the limits of error of the chemical analysis. A similar result was obtained with pure electrolytic iron, for which the same reaction-curves were obtained with both fine and coarse grain-sizes. From these experiments it is clear that the effect of varying grain-size on the position of the reaction-curve is negligible in comparison with the changes brought about by cold-working.

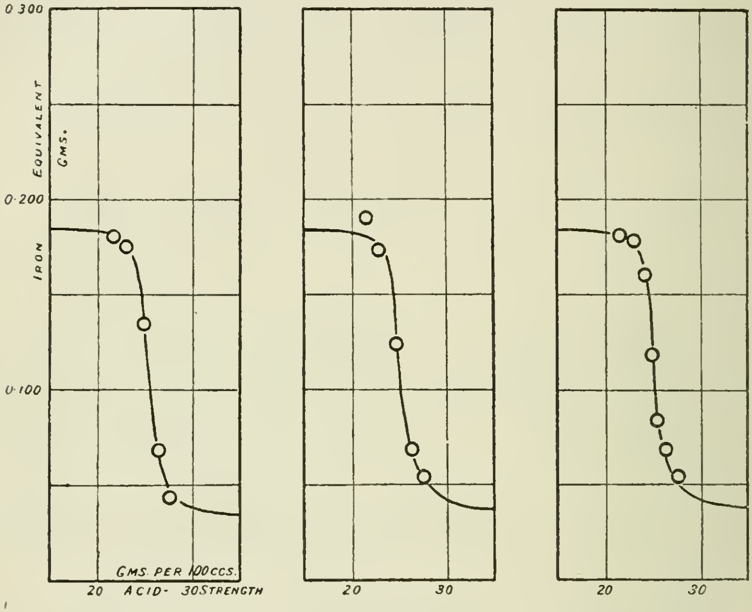

Fig. 26.—Photo 3. Fig. 27.—Photo 4. Fig. 28.—Photo 5.

Reaction-Curves of Pure Iron of varying Grain-size.

SUMMARY.

Part I.

1. The final reduction products obtained when iron is dissolved in dilute nitric acid are chiefly NO_2, NO, N_2, and NH_3, which are formed in amounts depending on the acid-strength ; in addition to this variation, the amounts are now found also to depend on the degree of cold-work in the sample.

2. A method is described for collecting and analysing the gases yielded by 0·30 gramme of sample dissolved at 100° C., and the primary and secondary reactions which occur are discussed ;

in particular the interchangeability of the N_2 with NH_3 and of NO with NO_2 is shown.

3. The reaction of pure iron undergoes an almost discontinuous change at a certain acid-strength (about 24 gms. per 100 c.c.), much of the $N_2 + NH_3$ being replaced by $NO + NO_2$ as the acid-strength increases from 23 to 25.

4. With iron the reaction products formed apparently depend on the concentration of NO_3, present as free acid or nitrate, and not on the acidity itself.

5. By plotting as ordinate the weight of iron consumed in forming $N_2 + NH_3$ and as abscissa the acid-strength as grammes per 100 c.c., a characteristic curve is obtained termed the "reaction-curve" which expresses the principal features of the reaction.

6. The reaction-curve of iron is slightly advanced by dissolving at lower temperatures.

Part II.

7. The relation between the position of the reaction curve, and the degree of strain in the sample is investigated in several typical cases, the curves being always shifted to the right with increasing strain.

8. Wires deformed by twisting yield progressively advancing reaction-curves. The energy used in twisting the wires is measured by a torsion spring.

9. Measurable changes in the gas-analysis are produced by an amount of energy which, if developed as heat, would not raise the material by 1·0° C.

10. Drawn wires yield similar curves; the relation of these changes to the reduction of area is examined.

11. For the interpretation of results, the reaction-curves to be derived from mixtures are considered, and the conclusions are tested experimentally for mixtures of ferrite with cementite and of ferrite with martensite; the reactions of cementite are discussed in detail. Deviations from the mixture-rule due to electrochemical action between different constituents in metallic contact have only a small effect in the case of iron and steel samples dissolved at 100° C.

12. The results for drawn and for twisted wires indicate that cold-working takes place in two stages, (1) the elastically strained crystal units are brought into an interlocked condition, (2) the crystal structure is then progressively broken up with the production of "amorphous material."

13. The method is used to investigate the removal of cold-work from iron by annealing; for the sample used the removal was found to be completed at 520° C.

14. Specimens of an annealed pure iron having widely differing grain-sizes give identical reaction-curves, indicating that the energy differences due to grain-size are too small to be detected by the method.

AN INVESTIGATION ON THE WEARING AND ANTIFRICTIONAL QUALITIES OF CAST IRON.[1]

(PRELIMINARY NOTE.)

By J. E. HURST (Acton).

The study of the wear of materials in general has of recent years become one of great importance. The extent of published work on this subject, in view of its great industrial importance, is, however, remarkably small, and relates chiefly to the wear of steels used for constructional purposes. Still less published information of the wearing properties of cast iron is to be found, and there does not appear to be any organised attempt at detailed investigation of this subject.

It has long been known to engineers that cast iron possesses unique and invaluable properties when used in the construction of the moving parts of machinery. In the construction of the wearing parts of machine tools and textile machinery it has been found by long experience that cast iron has no superior. Similarly in the construction of engine cylinders, particularly internal combustion engine cylinders, in spite of its many disadvantages, cast iron is still acknowledged to be the best material from the point of view of wearing and general running properties. Many other isolated examples could be quoted where cast iron has been used with striking success in the construction of machine parts requiring good wearing and antifrictional qualities.

The Wearing of Cast Iron.—Throughout this investigation wear will be defined as the loss in weight sustained by a substance when subjected to rubbing by another substance, over a given period of time, at a given speed, and under given pressure of contact. In the present state of knowledge of this subject, it is legitimate to assume that the mode in which the rubbing

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[1] Manuscript received March 20, 1918.

is performed will exert considerable influence on the ultimate wear, and there is no question that the ultimate extent of wear is considerably modified by the physical character of the rubbing agent. In this particular investigation the subject will, however, be strictly limited to those instances in which wear is brought about by the mutual rubbing of cast iron by cast iron under reciprocating sliding contact. This type of wear is chosen by reason of the fact that it more nearly approaches the actual conditions obtaining in engine cylinders.

The exact mechanism of wear in any given material is but little understood. In some recent investigations on the microstructure of worn gas-engine cylinder liner [1] surfaces, it has been qualitatively shown for the most part that wear in commercial grey cast iron is brought about by a process of surface disintegration. The surfaces of worn cast-iron cylinder specimens can be seen, on visual examination, to be covered with numerous holes, as illustrated in Fig. 1 (Plate III). These holes are the result of actual detachment of the crystal grains composing the surface A magnified view of such a hole, from which presumably a grain of phosphide eutectic has been detached, is shown in Fig. 2.

In a measure, wear of this nature would naturally be expected in such a material as cast iron, in view of the characteristic composite nature and intercrystalline brittleness of this alloy. It will, however, be readily appreciated that if this were the only cause at work in the production of wear, that once surface disintegration had commenced in cast iron, the subsequent rate of wear would rapidly increase, and on this assumption it would necessarily follow that the wearing qualities of cast iron would be decidedly poor. That this assumption is not borne out by practical experience is well known, and we are on practical grounds led to the conclusion that the rate of wear is not a simple function of surface disintegration alone. There is no doubt that there are several other factors at work in addition to surface disintegration, all of which combine to modify the total extent of wear. The plastic deformation of the constituent grains of the surface under the influence of the stresses produced is of immense importance, and undoubtedly plays a great part in modifying the extent of the wear.

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[1] J. E. Hurst, Manchester Association of Engineers, 1916.

It has been known to engineers for a considerable period, in connection with cast iron moving parts of machinery, that when these have been in use for a sufficient length of time to have acquired a peculiar glazed surface or glazed appearance, trouble with "galling" or "seizing" is practically eliminated, and the rate of wear would appear to diminish. Dealing[1] with friction clutches, it has been stated that "the coefficient of friction varies greatly with the state of the surfaces, and after the surfaces become glazed with use it drops away quickly."

Practical experience in connection with internal combustion engine pistons and cylinders confirms this conclusion. The cylinder walls in high-speed engines which have been running for a considerable period become glazed, harder, and considerably more difficult to file. It would appear that the object of some of the large continental gas-engine manufacturers in subjecting cylinders to a period of running in their engines previous to putting them in work, is in part to produce this glazed surface.

There is no doubt that this glazy appearance produced on cast iron surfaces after subjection to rubbing is due in some measure to the plastic deformation of the surface grains. Many instances have been met in connection with internal combustion engine cylinders in which layers of material can be distinctly seen to have flowed over the surface, filling up the hollows resulting from machine tool marking. These layers can be removed by careful polishing and etching and the underlying machine tool marks thus revealed. The unetched surfaces of worn engine cylinders under the microscope very frequently present a very finely divided granular structure in which the hard particles of phosphide eutectic can be seen standing in relief. It is believed that this granular type structure is the result of plastic deformation of the surface grains.

The debris resulting from the surface disintegration of the cast iron is a factor of considerable importance in industrial cases of wear.

In the particular case of engine cylinders, the debris becomes suspended in the film of lubricant, and in this condition most probably acts as a polishing agent whereby the relief polishing effect observed in the micro-examination of worn liner surfaces is brought about. This effect is also well illustrated in Fig. 2. It is an open question whether this debris is in any way connected with the glazy appearance observed on liner surfaces already mentioned.

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[1] W. C. Gass, Manchester Association of Engineers, 1916.

In speaking of the old-fashioned copper-faced friction clutches, Gass[1] states that "examination of the surface of the copper after long work showed that the surface was embedded with fine particles of iron from the outer part of the cone or clutch, and it (the surface) became hard and glazed."

Many cases of galling or seizure of the piston and the liner are known to engine manufacturers which cannot be easily accounted for by the tightness of the piston, or alignment of the engine, or any other mechanical features. In the author's experience, such seizures very frequently take place shortly after the cylinder or liner has been put in work, and are for the most part encountered in those cylinders consisting of very open-grained cast irons. Such cases of seizure are most probably due to the excessive amount of debris produced as a result of surface disintegration. The amount produced is so large that the friction set up as a result of its presence develops momentarily sufficient local heat to melt this debris. It can actually be observed as a white heat. On taking out the piston, the layer of material pasted on to the side of the liner can be plainly seen and is perfectly glass hard.

In general, in such cases of sliding friction as engine cylinders, a large amount of debris is eventually pushed out along with the oil. It is quite possible that some of the material becomes rubbed into the wearing surfaces. This is a matter for investigation.

An interesting example of the "rolling in" of debris into the wearing surface of cast iron has been recently met with. This is the case of a large flywheel lathe face plate. This lathe was used for the turning of extra heavy flywheels upwards of 12 tons in weight. The larger portion of this load was taken up by two hardened steel rollers, as shown in the diagram (Fig. 3). The whole of the circumferential face, which was about 12 inches in width, was originally machined. After being in use for a matter of upwards of eight years, a band round this face was worn some $\frac{3}{16}$ inch deep, the width of the rollers, as shown in the photograph Fig. 4. The whole of the surface of this depression presented a distinctly disintegrated appearance, and was found to be covered with flakes of material distinctly having the appearance of being rolled in. These flakes could easily be detached by holding a blunt-edged tool against the rotating surface. Some of these flakes were collected and analysed, with the following results :

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[1] *Loc. cit.*

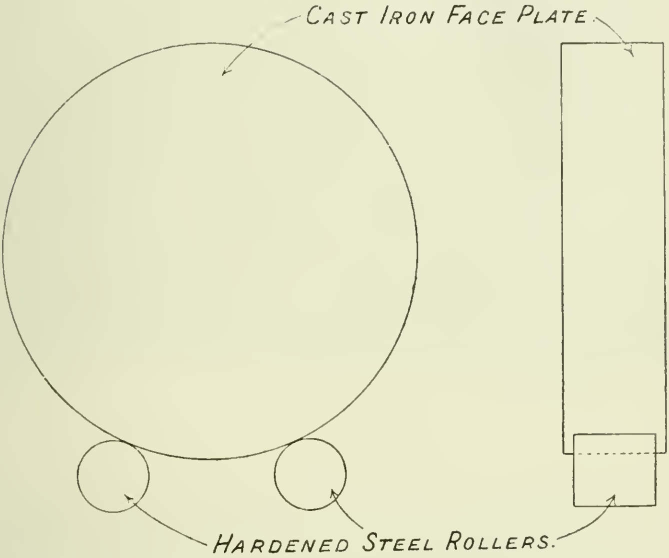

FIG. 3.

	Per Cent.
Combined carbon	nil
Graphite	3·49
Total carbon	3·48 by combustion.
Silicon	2·66
Manganese	0·99
Phosphorus	0·79

These flakes are undoubtedly debris resulting from wear which has been actually rolled into the surface. In this particular instance it is also possible that a certain amount of dust arising from the cast iron turnings falling into the pit beneath the face plate may collect on this face and also be rolled into the surface. Unfortunately the author has no chemical analysis of the actual plate, but from the pig irons used in the mixture it is certain that the phosphorus content is higher than that given for the flakes themselves, and is probably in the region of 1 per cent. This would suggest that a considerable quantity of the phosphide constituent has escaped rolling in and probably fallen away from the plate. This is an interesting feature.

The extent to which these layers of rolled-in material may form is clearly illustrated by this example.

Surface Finish.—In the light of the above, it will be clearly obvious in industrial practice, and also for the purposes of this investigation, that the character of the finish of the surface of the cast iron will be of great importance.

It will be readily appreciated that the state of the surface finish will exert a profound influence in determining the initial rate of wear of the cylinder. A roughly finished liner wears initially very rapidly, and there are undoubtedly many cases of seizure of gas-engines which, if thoroughly investigated, could be largely attributed to the rapid production of debris as a result of the rapid initial wear due to a comparatively rough, machined surface.

In the second place, cast iron, owing to its relatively brittle nature due to its low intercrystalline strength, is far more sensitive to the stresses set up during machining than most metals. Consequently with rough and severe machining the surface of cast iron becomes undoubtedly badly disintegrated and distorted and full of crystalline cracks which may extend to a considerable distance into the cast iron, far below the actual surface. This will undoubtedly tend to increase the wear by surface disintegration owing to the partial loosening of the crystal grains.

It is probably due in a large measure to these reasons that an internally ground surface is far more satisfactory than an ordinary machined surface on cast iron Diesel engine liners.

It will readily be appreciated that the extent of the damage done to cast iron surfaces as a result of machining will vary in different cast irons, and will be largely a function of the tensile strength (or intercrystalline cohesion). Suffice it to say that it is of paramount importance in the study of wearing phenomena in cast iron to ensure a standard form of "surface finish" on all specimens for investigation purposes.

Mechanical Properties.—In actual practice it is frequently

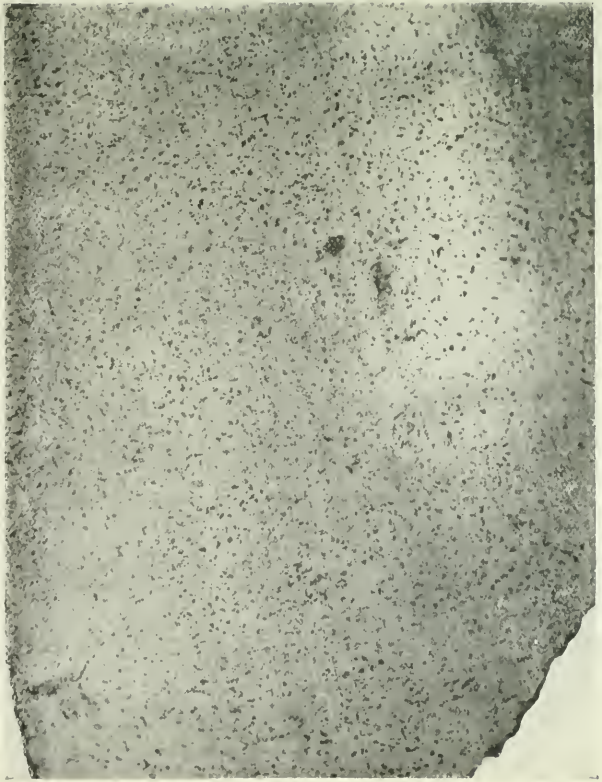

Fig. 1.—Surface of worn Gas Engine Cylinder Liner.
Somewhat reduced

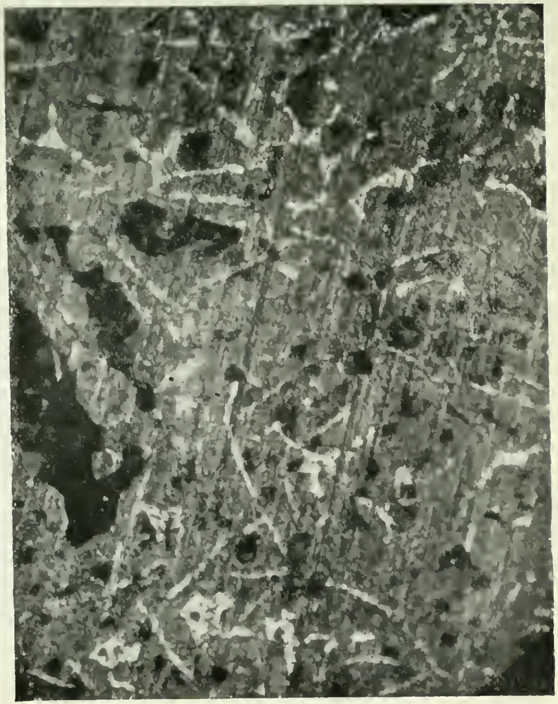

Fig. 2.—Magnified Surface of worn Gas Engine Cylinder Liner, showing holes representing detached constituents.
× 150 diams. Not etched.

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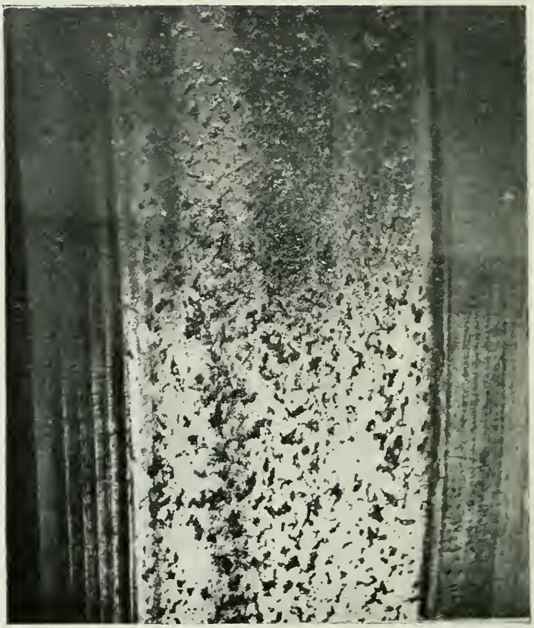

Fig. 4.—Worn Rolling Face of Lathe Faceplate.
Considerably reduced.

very difficult to correlate the various mechanical properties with the wearing properties as indicated by actual use. In view of the peculiar nature of cast iron, this is more or less what would be expected. Cast iron, it must be remembered, is a conglomeration of constituents of widely varying mechanical properties, separated at their individual boundaries by graphite plates. On this account, consequently, the mechanical properties of the alloys, when considered as a whole, bear no definite relation to those of even the majority of its constituent grains, and also they (the mechanical properties) are very sensitive to slight variations in structural arrangement. It is perfectly legitimate to conclude that the character of the constituent grains of the cast iron exert considerable influence on the wearing properties, and it will therefore be obvious that the comparison of mechanical properties alone, unaccompanied by some idea of the structural components and arrangement, is very unsatisfactory. In this respect cast iron is entirely different to other well-known alloys. An attempt at determining the relation between the mechanical properties of cast iron and wear is that contained in a pamphlet issued by Messrs. Ludwig Loewe & Co., Ltd. In these experiments wear was determined as the loss in weight sustained by a specimen of

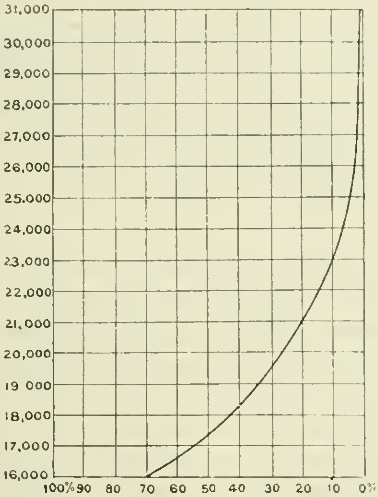

FIG. 5.—Relation between Tensile Strength and Wear (Loewe).

cast iron on rubbing at a given speed and under a given load in contact with a hardened steel die. The loss in weight sustained after rubbing for a given period of time was plotted against the tensile strength, and the resulting curve is shown in Fig. 6. It will be seen that a perfectly smooth curve is obtained, and the extent of the wearing bears some relation to the tensile strength.

Unfortunately, so far as the author is aware, no data were included in these experiments respecting the chemical composition and microstructure of the specimens tested. The period over which the rubbing took place, and the influence of debris resulting from the surface disintegration, are also important factors, and it would not appear that any special attempt was made in this research to determine the influence of these factors.

The period over which the rubbing took place and the character of the " finish " of the specimens is of considerable importance. From what has already been said it may be assumed that in the initial stages of wear the influence of surface disintegration is predominant.

It is important to note that the rate of wear, as measured by the slope of the curve, is much greater and faster with the lower tensile strength irons. This is very probably due to the fact that the lower tensile strength irons are more readily liable to surface disintegration. The extent of wear in the lower tensile iron in this investigation is very large, amounting to 70 per cent. of the total weight of the specimen. Some idea of the structural arrangement of these irons would have been of considerable value.

Hardness and Wear.—From a long series of records of observations on the relation between the Brinell hardness and the behaviour of cast iron for the purposes of engine-cylinder construction, it can only be concluded that the Brinell hardness numeral bears no simple relation to the wearing qualities, and hence this numeral is little guide to the nature of these qualities. Cast irons having the same hardness numeral frequently wear at widely different rates, and softer cast irons frequently wear longer and better than harder ones, and *vice versa,* under, so far as can be judged, identical industrial conditions. Several instances illustrating the unsatisfactory nature of the Brinell hardness numeral in this connection are abstracted from amongst a large collection of similar cases in Table I.

The problem of the relation of the Brinell hardness numeral

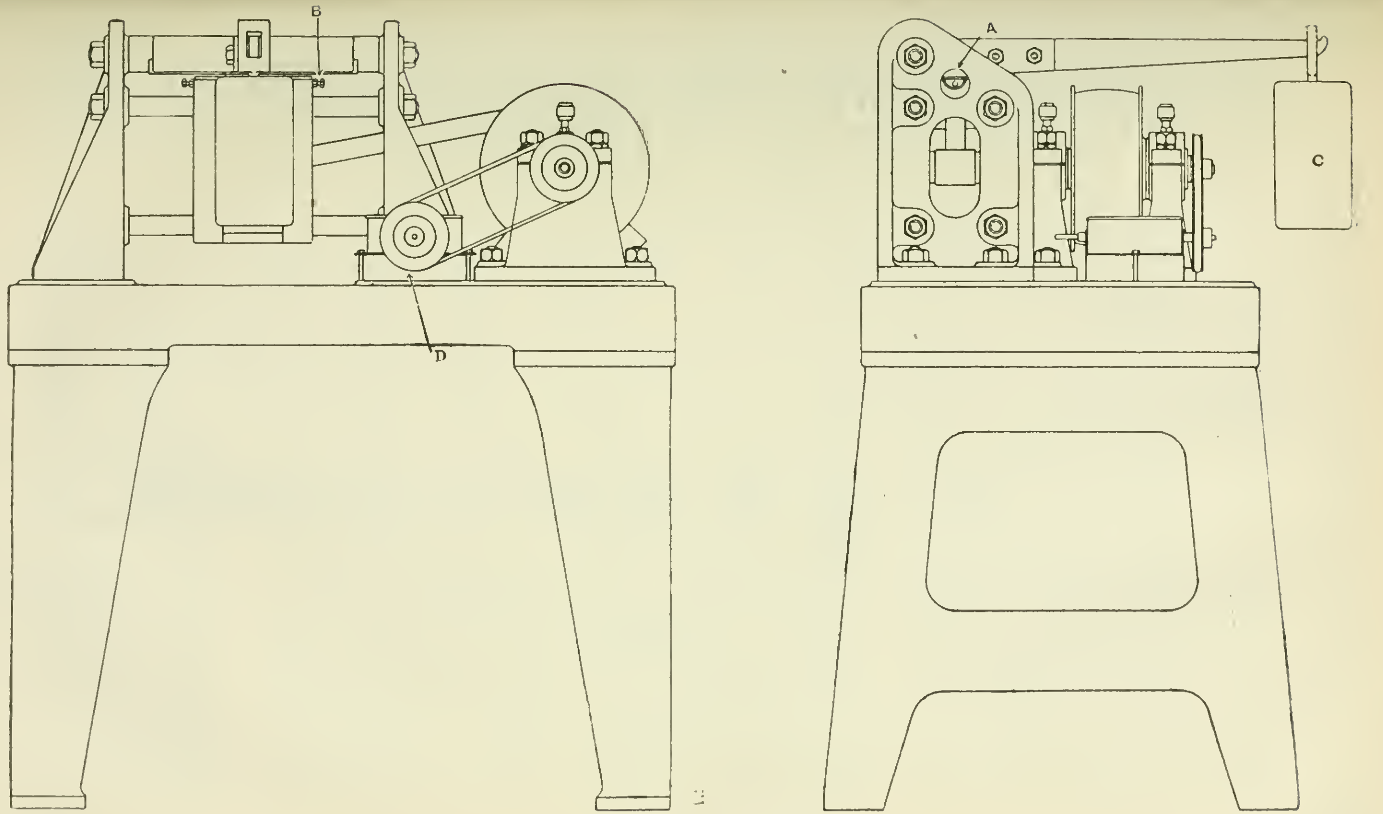

Fig. 6.—Side and End Elevation.

TABLE I.

Test No.	Analysis.							Thickness of Casting.	Brinell. No.		Remarks.
	Combined Carbon per Cent.	Graphite per Cent.	Total Carbon per Cent.	Silicon per Cent.	Manganese per Cent.	Sulphur per Cent.	Phosphorus per Cent.		Inside,	Out-side.	
N2·0	0·40	2·67	3·07	2·28	0·76	0·09	1·10	1 inch	163	170	Ran well with very little wear.
N2·1	0·40	2·67	3·07	2·28	0·77			1 ,,	179–149	187	,, ,, ,,
N2·9	0·50	3·08	3·63	2·28	0·93			1⅛ ,,	187	196	Ran badly and wore quickly.
4·81	0·58	2·86	3·44	1·68	1·03	...	1·58	¾ ,,	228	228	,, ,, ,,
0·4C.	0·87	2·46	3·33	0·98	1·10	0·09	0·89	1 ,,	228	228	Good wearing liner.

to wear in connection with the metal cast iron is rendered considerably more complex by the uncertain relation of the numeral both to the chemical constitution and to the other mechanical properties of this metal. It must always be borne in mind that the hardness numerals of cast iron alloys are only comparative, and that only when cast under strictly identical conditions. Apart from the chemical constitution, the Brinell hardness is dependent on the size and distribution of the structural components of the cast iron, which may vary considerably in any given alloy within wide limits. The size and distribution of the structural components is dependent on a number of factors, amongst which the casting temperature and the rate of cooling are of the greatest importance.

Again, the chemical constitution may vary considerably without any appreciable effect on the hardness numeral. This is very important from the point of view that variations in chemical composition which are known to exert considerable influence on the wearing properties may occur without any indication being made apparent by the Brinell figure. For example, it is possible to have two cast irons of practically the same hardness numeral varying considerably in, say, phosphorus or manganese. It is certain that the wearing properties of these irons will vary considerably. The influence of casting temperature is of considerable importance in a research of this nature, as is well illustrated by the results in Table II. These samples were cast under strictly comparable conditions from cupola iron, and the variation in Brinell hardness observed is very striking. The average hardness of the fairly low phosphorus sample, as would be expected, is considerably below that of the higher phosphorus samples, yet with a sufficiently high casting temperature the low phosphorus sample is rendered as high as that of the hardest samples. (The casting temperatures were registered by the Mésuré or Nouel type optical pyrometer.)

It is legitimate to conclude from these experiments that this variation in the Brinell figure is largely directly caused by variations in the structural arrangement due to the influence of casting temperature. Though such variations in structure are difficult to determine under the microscope, this will readily be appreciated as all the more reason why the influence of this factor must be

TABLE II.

Test No.	Analyses.							Casting Temperature. Degrees C.	Tensile Strength. Tons per Square Inch.	Brinell Hardness.[1]	Average Brinell.	Remarks.
	Combined Carbon per Cent.	Graphite per Cent.	Total Carbon per Cent.	Silicon per Cent.	Manganese per Cent.	Sulphur per Cent.	Phosphorus per Cent.					
1	0·44	2·97	3·41	...	...	...	...	1320	Defec.	228	212	
2	0·37	2·80	3·17	...	...	...	...	1300	10·5	217		
3	0·38	3·02	3·40	...	...	...	...	1250	10·7	196		
4	0·35	3·00	3·35	2·24	0·71	0·137	1·84	1190	11·0	207		
5	0·45	3·21	3·66	1·86	0·93	0·11	1·00	1300	12·8	241	226·5	
6	0·43	2·96	3·39	...	...	...	...	1250	13·0	196		
7	0·40	2·63	3·03	...	...	...	...	1200	10·65	241		
8	0·46	2·65	3·11	...	...	...	...	1190	10·7	228		Did not fill mould.
9	0·50	2·66	3·16	1·73	0·72	0·12	0·68	1360	12·8	241	196	
10	0·50	2·45	2·95	...	...	...	...	1290	13·4	196		
11	0·51	2·27	2·78	...	...	...	...	1250	11·85	137		
12	0·55	2·50	3·05	...	...	...	...	1190	13·2	196		Hardly run.

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[1] Average of twelve readings. Blast-pressure = 17-inch water-gauge.

rendered strictly comparative in an investigation of this nature. Likewise, needless to say, every precaution has been taken with regard to the effect of rate of cooling.

Chemical Constitution.—So far as the author is aware, there has been no organised research published on the influence of varying amounts of the constituents present on the behaviour of cast iron under wear. The investigation of this portion of the subject is one of the main objects of this research. The influence of manganese in increasing the resistance to wear appears to have long been known, and in a lesser degree the influence of chromium. It has frequently been stated that this influence on the part of manganese is due to the tendency conferred upon cast iron by this constituent to produce under the influence of wear the peculiar glazy surface. Practical experience would appear to confirm this statement, and it will be obvious that the condition in which the manganese exists, whether as the sulphide of manganese or in the solid solution, and its resolution products will have considerable bearing upon its influence.

We have no exact information concerning the influence of varying quantities of combined and free carbon, silicon, and phosphorus on the wearing properties of cast iron.

Microstructure.—The relation between the chemical and structural constitution of cast iron is very intimate, and it may be anticipated that the influence of chemical composition on the wearing properties of cast iron will be indirectly connected with the microstructure. In any case, particularly in work of this nature, the chemical and structural constitution cannot be considered separately. From previous considerations it will readily be appreciated that the structural constitution of cast iron plays a very important part in determining the extent of its wear under given circumstances. Very little actual investigation on this aspect of the subject, which is one of the prime objects of this research, appears to have been published.

Anti-Frictional Qualities.—It is a well-known fact that cast iron behaves at least as satisfactorily as, if not more satisfactorily than, most other metals or alloys from the point of view of overheating and seizing when employed in any capacity in which it has to resist wear. Cast iron can for this reason be legitimately classed alongside the so-called anti-frictional alloys or bearing metals—tin, lead, antimony, and copper. These alloys are so designed, as a result largely of experience, to give the most satisfactory results when in use as engine or lineshaft bearings. In fact, the latter type of bearings are nowadays very frequently manufactured of ordinary grey commerical cast iron, and are being used with far more satisfactory results than any of the usual anti-frictional or bearing metals.

Whether this "quality" of cast iron can be strictly defined as a true property it is as yet difficult to say. It yet remains to determine accurately the factors upon which the quality depends.

Experience with the so-called anti-frictional alloys has shown that such an alloy should consist of at least two constituents of widely different physical properties embedded in each other. The soft constituent confers upon the alloy the necessary degree of plasticity, whilst the presence of the hard constituent raises the critical pressure which produces the sudden increase in the coefficient of friction.[1] When in actual use the surface of these alloys is worn in such a manner as to produce a surface of an irregular contour, the harder portions standing in relief. The minute depressions over the surface of the bearing metal in actual use can be considered to serve as minute reservoirs which preserve an effective distribution of lubricant over the whole of the bearing surface.

It seems very probable that the excellent anti-frictional properties of cast iron may in a large measure be due to the structural character of the cast iron. Cast iron contains the necessary hard constituents embedded in a softer matrix which under certain conditions may exhibit very definite cellular arrangements which are undoubtedly in a large measure responsible for the excellent anti-frictional properties.

It is maintained by many that the lubricating qualities of the free graphite present in cast iron are likewise largely responsible for the excellence of these qualities. According to Acheson, "it has been found [2] after many exhaustive tests that 0·35 per cent. of colloidal graphite properly diffused is sufficient to confer exceptional lubricating qualities in the oil. Even though such a small quantity of graphite be responsible for a marked increase in the excellence of the lubricating qualities of oil, it is difficult to conceive how the small amount of graphite in the superficial layers of cast iron cylinders can account for the excellence of their anti-frictional properties over the very long period of time some of these cylinders are in actual use.

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[1] E. F. Law, "Alloys."

[2] W. W. Acheson, Junr., *Chemical News*, July 16, 1915.

It is undoubted that the glazy surfaces produced on cast iron after subjection to wear also in a large measure influence the anti-frictional qualities. This fact has already been indicated, and further investigation of this is of great importance. Special attention will be given to the formation and influence of the "glazed surface" throughout this research.

It is important to note that certain manufacturers using cast iron for lineshaft bearings subject the cast iron to a preliminary annealing treatment. Manufacturers of textile machinery in a like manner anneal all cast iron spindles. It is claimed that by this means both the wearing and anti-frictional qualities are improved, although in the case of the textile-machinery manufacturer, machining considerations enter largely into the question. It is by no means obvious why annealing before use should improve the cast iron from this particular point of view, and further investigation into this aspect of the subject is necessary.

Objects of this Investigation.—The main object of this investigation, in the first place, is to determine the extent of the influence of variations in the chemical and structural constitution on rate and extent of wear. Incidentally it is hoped to obtain considerable information on the relation between the mechanical properties and wear and also on the anti-frictional properties.

A machine has been designed and is in course of construction for the purpose of carrying out the wear tests. This is illustrated on Fig. 6. In this machine the specimen held in the lever at "A" is subjected to the wearing action of another specimen of the same material gripped in the reciprocating crosshead at "B." The load on the specimen can be applied by means of weights at the end of the lever arm "C," and the revolutions of the crank are counted by the rotary engine counter "D." The chief reasons for choosing a reciprocating motion are as follows:

1. It more nearly approximates the industrial conditions obtaining in an engine cylinder.
2. It allows of the employment of flat-faced specimens, which are more convenient for microscopic examination.

The machine has been designed sufficiently rigid, and it is not intended to run at very high speeds, in order that vibration shall not be excessive. The extent of wear will be determined by weighing the specimen before and after each experiment. Provision is also being made (in the machine under construction) for using water-cooled specimens and studying the effect of the addition of lubricant (not shown in figure). In addition in the machine as shown in the figure the specimens are shown gripped in cylindrical seatings allowing of lateral self-adjustment of the two wearing faces. This is being substituted by a special spherical seating allowing of universal self-adjustment.

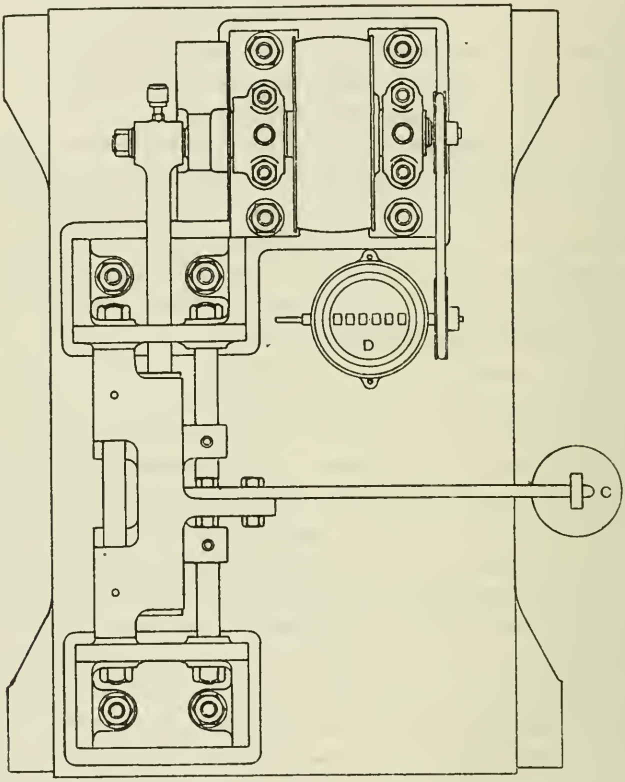
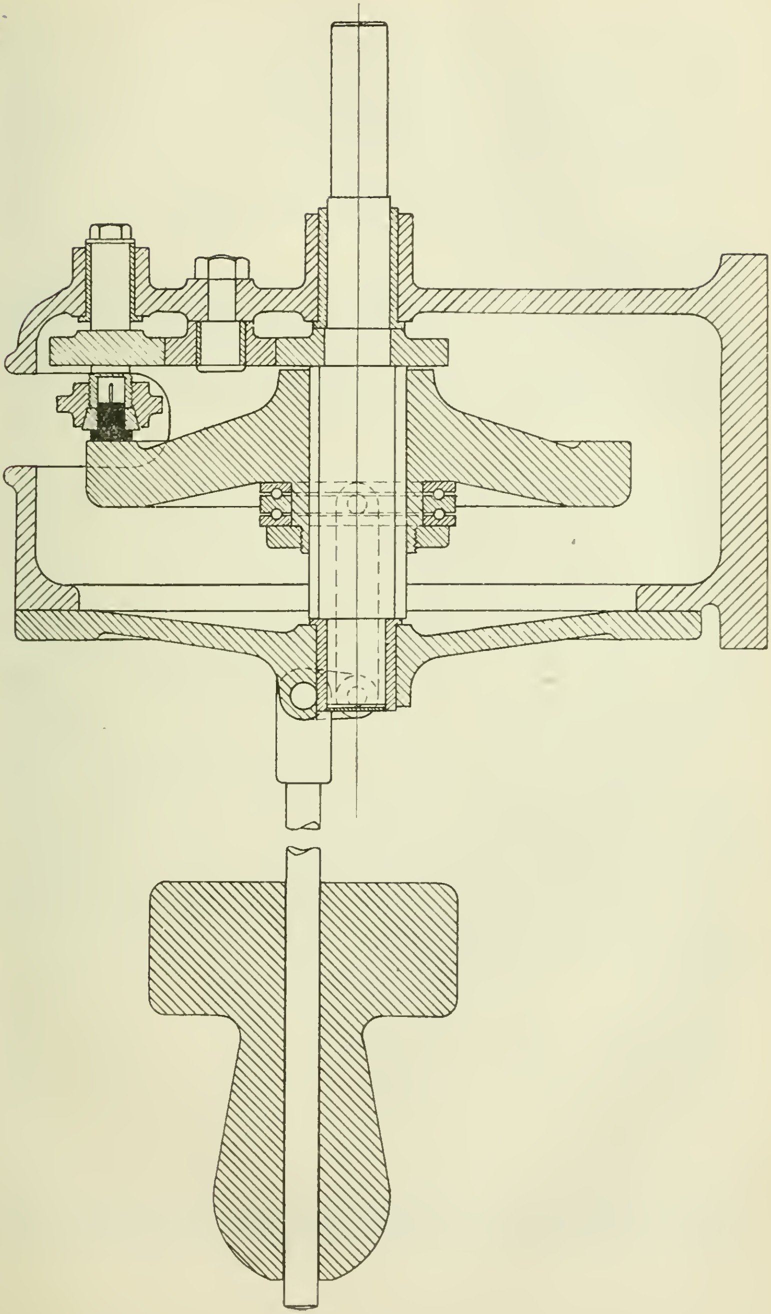


Fig. 7.

A second machine is also being constructed on the lines indicated in Fig. 7. In this machine a small specimen is pressed



against a standard cast iron rotating disc by means of a definite load. The size of the specimen is very small in comparison to that of the disc, thus rendering the speed of the disc at any point on the contact area of the specimen being substantially the same. The specimen itself will also be given a slow rotating movement, thus subjecting the specimen to a motion very much akin to the reciprocating motion. This machine has been designed to run at high speeds and is intended for the rapid testing of small specimens.

The author begs to acknowledge his most sincere thanks to Mr. Tomlinson, of the National Physical Laboratory, for the suggestion of this second type of machine, and also for the universal joint mentioned in the previous machine. These two machines are both under construction.

Specimens.—A complete series of bars have been prepared, the compositions of which have been so arranged as to obtain complete series of alloys varying in each constituent over the ranges commonly met with in industrial practice. Special precautions were taken during the casting to ensure as far as possible strict comparability. The metal was obtained by melting a hæmatite pig in a 200-lb. plumbago crucible in a coke-fired melting furnace. The desired compositions were obtained by the addition of foundry pig and ferro-alloys. The casting temperatures of the bars were observed and arranged in most cases as nearly identical as possible. In all cases the test-bars, which were of the following dimensions, 12 inches × $1\frac{1}{8}$ inch × $1\frac{1}{8}$ inch, were allowed to cool out completely in the moulding-box.

The complete chemical analyses, mechanical tests, and micro-structural measurements of these bars are being prepared.

THE PROTECTION OF IRON WITH PAINT AGAINST ATMOSPHERIC CORROSION.[1]

By J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. (Worcester),
Temporary Captain, Royal Engineers.

With the ever-increasing application of iron and steel for structural purposes, the problem of determining the best methods of arresting corrosion rises continuously in importance. For most ordinary purposes special steels cannot be employed, both on account of their prohibitive cost and their peculiar physical properties. There remain, therefore, two directions in which a solution to the problem may be sought, namely, (1) by reducing the corrosivity of the media in which the metal is placed, and (2) by application of a protective coating to the metal, which shall prevent its coming into direct contact with corrosive agencies.

The former of these methods is frequently applied in protecting water-pipes from internal corrosion, the water being rendered more or less innocuous by lime treatment.[2] The second method has been attempted in a variety of ways, such as, for example, the employment of cement, tinning, galvanising, superficial oxidation or phosphorisation of the metal, and painting.

The present research deals with the last of these, and has been undertaken, not so much with the object of discovering the best paint mixture for the purpose in hand, as to determine the broad principles governing the successful mixing and application of paint to iron.

In carrying out his work the painter has usually two objectives in view, namely, the protective and the ornate. In the painting of iron work in protected interiors the question of corrosion is usually subsidiary, since serious rusting is hardly likely to occur whatever the kind of paint employed. Considerable attention may in such circumstances be safely bestowed upon the ornamen-

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[1] Received February 5, 1918. Presented at the Annual Meeting of the Institute, May 2–3, 1918.

[2] This method has proved very successful in checking the internal corrosion suffered by the main water-supply pipes connecting Mundaring reservoir with Kalgoorlie in Western Australia—a distance of some 350 miles. See Binnie, "The Corrosion of Iron and Steel Water-Pipes," a paper read before the Institute of Sanitary Engineers, Westminster, April 1915.

tal properties of the paint. External structures, such as bridges, on the other hand, require careful protection from the corrosive action of the weather, and if ornamentation is considered at all, it is generally quite subsidiary to preservation.

Choice of Experimental Methods.

The value of research work depends not merely upon the accuracy of the worker, but also upon the method adopted for arriving at the results. The object of the present research is to arrive at results of technical and practical value rather than of academic interest. The method of research must therefore be adapted accordingly. The amount of work done on the problem now under discussion is remarkably small in comparison with the importance of the subject. It seems desirable, therefore, to pass briefly in review the different experimental methods adopted by various workers in this field, pointing out their valuable features and criticising their limitations.

Several ingenious methods have been devised for testing within a few hours the protective efficiency of a coat of paint. Loesner [1] recommends the painting of small strips of iron, and laying them, when dried, over a water-bath, supported by two pieces of wood to prevent mechanical injury. The bath is filled with water up to 2 inches below the strips of metal, and maintained at the boiling point for fifteen hours. The strips are removed, the paint loosened with aniline, and the metal examined for rust.

Identical in principle with the foregoing is the method adopted by Liebreich[2] and Spitzer, who painted small iron plates, measuring 9 × 12 centimetres, in air, and suspended them, when the paint had set, vertically from glass rods in pails of water, maintained continuously at the boiling point for ninety-six hours. At the conclusion of the tests photographs were taken to render the observations permanent. No quantitative physical measurements were attempted, although the results could easily be made quantitative by cleaning the plates and determining the loss in weight through the removal of rust.

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[1] Loesner, *Chemische Revue*, vol. xxiv. p. 329.

[2] Liebreich and Spitzer, *Zeitsch. Elektrochem.*, 1912, vol. xviii. p. 94.

Dubois[1] pickled his plates in acid and washed them in caustic soda, after which they were rinsed, dried, and coated with the desired mixtures. When the oil had set the plates were exposed in a box to oxygen and corroding gases kept moist with a little steam. After stated intervals the plates were examined for corrosion, photographs being taken to render the observations permanent. The size of the plates is not stated, and no weighings were made, although such could easily be done as suggested for the previous method.

Not a few investigators are in favour of electrical methods, as these are both rapid and admit of accurate quantitative measurement.

Benson[2] and Pollock recommend the use of small iron plates measuring 1 × 1·4 inches in area. These are attached to copper wire, and after painting are immersed in an electrolyte to constitute the anode. A cathode of platinum is introduced, and a direct current of 8 volts pressure is passed continuously through. Clearly the conductivity will increase as the paint disintegrates, and a quantitative measure is thus forthcoming for the protective efficiency of the coating. Experiment shows that, under these conditions, useful comparative results may be obtained in six hours.

Walker[3] and Lewis called attention to the fact that fruit cans lacquered with a high-grade copal linseed oil varnish corroded more seriously than the unprotected metal, and attributed this to the depolarising action of the unsaturated linoxyn compounds. These absorbed the protecting films of hydrogen produced by the acid fruit liquors upon the metal, thus exposing the latter to further attack. The authors therefore devised a cell for determining the resistance of a paint film. It consisted of a U-tube containing potassium chloride solution. Into one limb was inserted a coil of iron wire to serve as anode, and into the other a longer spiral of iron wire, which had previously been dipped in paint and allowed to set, to serve as cathode. The current passing was measured by a chemical voltameter, and was proportional to the time until the film broke down.

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[1] Dubois, *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. p. 968.

[2] Benson and Pollock, *ibid.*, 1911, vol. iii. p. 670.

[3] Walker and Lewis, *ibid.*, 1909, vol. i. p. 754.

This method has been developed by Slade,[1] and may be applied to considerable numbers of paint films at one and the same time. The tests are complete in about 300 hours.

Each of the foregoing acceleration tests possesses two great advantages, namely, rapidity and ease of quantitative measurement. The question arises, however, as to whether or not the results obtained afford a correct indication of the efficiency of paint films under actual working conditions. If they do, then the present author is inclined to regard the electrical methods as extremely valuable. But the data at our disposal do not suffice to admit of drawing such a conclusion. In recent communications to this Journal it has been repeatedly proved that acceleration tests for determining the corrodibility of iron yield entirely untrustworthy results, and that the only reliable data are those obtained by experimenting under conditions approximating as closely as possible to those to which the metal will be subjected in practice.

Now since in the tests under consideration the efficiency of the paint film is measured either directly or indirectly by the corrosion of the underlying metal, the present author has very serious misgivings as to the value of any results obtained by acceleration methods. It appeared to him wiser to adopt the slow and arduous process of imitating working conditions in a series of field tests rather than to rapidly accumulate a volume of data of doubtful practical utility.

A few field tests had already been carried out by the author in 1911,[2] and the results communicated to this Journal in the two succeeding years. The method consisted in exposing plates to the atmosphere for several months, and noting their alteration in appearance and weight. The plates measured 1 × 1½ feet in area, were pickled in dilute sulphuric acid to remove the scale, washed in caustic soda, and finally scrubbed in flowing water and dried at 100° C. After weighing and painting they were suspended to a specially constructed wooden fence for several months, and when corrosion had proceeded to a sufficient extent, the plates were graded according to their appearance, then cleaned and re-weighed. The loss in weight gave a quantitative measure

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[1] Slade, *Journal of Industrial and Engineering Chemistry*, 1912, vol. iv. p. 189.

[2] Friend, *Carnegie Scholarship Memoirs*, 1912, vol. iv.; 1913, vol. v.

(Newton Friend.)

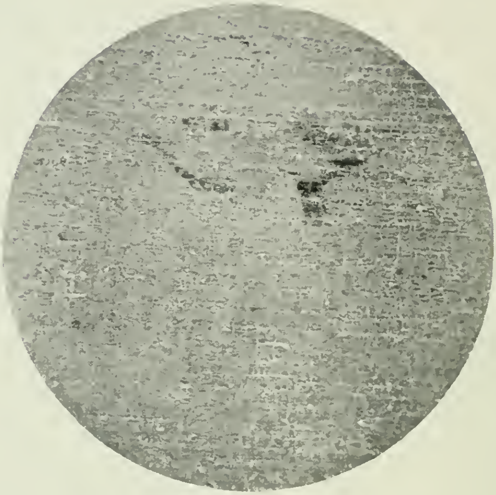
PLATE V.

EXPERIMENTAL PLATES AT WORCESTER.

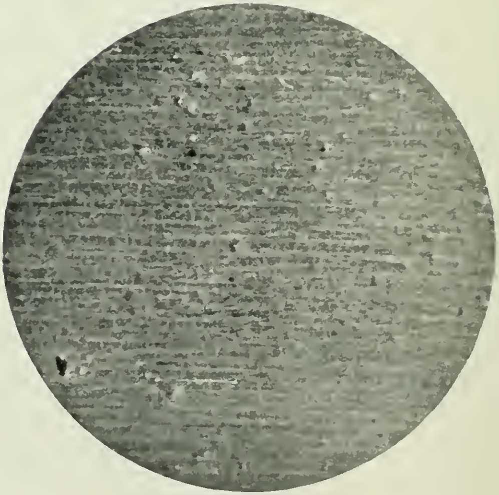
[*To face p.* 80

(*Newton Friend.*)

PLATE VI.



Yellow.



Red.

of the corrosion, and it was observed that this latter figure did not always correspond to the appearance of the plates.

This method suffers from two disadvantages, namely, its extreme slowness, and the difficulty of determining with accuracy the small differences in weight of the heavy plates as the result of corrosion. The former of these is purely a question of time and patience; nevertheless, it would seldom be practicable to hold up painting in commercial life for several years whilst experiments were carried out as to the best kind of paint to use. It was thought that results of equal value might be somewhat more rapidly obtained by total immersion of painted plates in water. Tests were accordingly carried out in large wooden tanks with plates 10 inches square. The results obtained in this way, however, did not always harmonise with those of the preceding method, apparently indicating that varying conditions require proportionately different treatment—a very strong argument against acceleration tests.

Walker [1] and Voorhees, in an excellent piece of research, suspended their plates in tanks, which were alternately filled with water and emptied. Corrosion is very appreciably accelerated in this way, but it has not yet been demonstrated that the same kind of results are obtained as by prolonged exposure to the atmosphere. On theoretical grounds intermediate results between atmospheric and total immersion might be expected. The second disadvantage, namely, the difficulty of determining with accuracy the small differences in weight of heavy metal plates as the result of corrosion, is really serious, and has led not a few investigators to discard the weighing altogether.[2] Estimates of the value of the protective coats of paint are, in these cases, made by a careful examination of their surfaces. This method was adopted in connection with a comprehensive series of tests begun in 1908 near Atlantic City, N.J., under the ægis of Committee U of the American Society for Testing Materials.[3] Several hundred plates were painted with different mixtures and exposed to weathering on a series of wooden fences. When inspecting the surfaces after the lapse of various intervals of time careful note was taken of any obvious superficial changes, such as chalking, change of colour, loss of opacity, disintegration of the paint film, &c. Permanent records were made with the aid of a photomicroscope, which rendered easy the detection of cracks and minute abrasions. The observations enabled the paints to be graded in an order of efficiency comprising ten classes, the tenth rating offering the best protection, and the zero rating the least.

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[1] Walker and Voorhees, *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. p. 899.

[2] See Walker and Voorhees, *loc. cit.*

[3] See Cushman and Gardner, "Corrosion and Preservation of Iron and Steel" (New York, 1910). Gardner, "Paint Technology and Paints" (New York, 1911).

As the authors themselves point out,[1] however, "it must be apparent that although a paint film may be opaque, corrosion goes on underneath for a long time before the trouble becomes evident on the surface. A time comes, however, when little blisters make their appearance on the film. This appearance is a preliminary step to the breaking out of the tubercles of rust which are so familiar to all observers."

This, in the present author's opinion, constitutes a serious weakness in an otherwise excellent method. In the preliminary experiments referred to above,[2] it was observed that "the surface of the paint film does not always give a correct idea as to the extent of corrosion."

Conclusions.—The foregoing considerations lead to the following conclusions:

1. The practical value of acceleration tests is uncertain in the present state of our knowledge.

2. It seems desirable to carry out extensive. field tests with painted plates under at least four different conditions, namely:

(*a*) Prolonged exposure to the weather—for information concerning the painting of aerial work.
(*b*) Total immersion in sea water—for marine purposes.
(*c*) Total immersion in river water, and
(*d*) Alternate wet and dry.

The present memoir is concerned with the first of these field tests, namely, prolonged exposure to the weather.

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[1] Cushman and Gardner, *op. cit.*, p. 193.

[2] Friend, *Carnegie Scholarship Memoirs*, 1912, vol. iv.

Special Features of the Work.

The factors involved in the painting of iron are quite distinct from those where wood is concerned, the main points of difference being as follows:

1. Wood is porous and absorbent, consequently a relatively lavish coat of thin paint may be applied at first. The oil sinks into the wood and the paint becomes in consequence firmly attached. Iron, on the other hand, is non-absorbent, and a thin paint, if applied lavishly, tends to run and to crinkle on setting. Furthermore, if the surface of the metal is very smooth, the paint has considerable difficulty in gripping it, and is liable to be rubbed off the more easily by mechanical wear.

2. The expansion of iron with rise of temperature is much more pronounced than that of wood in similar circumstances. Hence a more elastic paint is desirable for the metal.

3. It may generally be assumed that, so long as the coating of paint remains good, the wood beneath will not undergo any very material change. In the case of iron, however, owing to the permeability of paint to oxygen and water vapour, the underlying metal may suffer considerable corrosion even whilst the surface paint is in good condition. The expansion caused by the rusting will raise the paint film slightly from the metallic surface, thereby enabling further serious corrosion to take place unobserved. When the paint ultimately disintegrates it peels off in large pieces and exposes the deteriorated metal. Whilst, therefore, woodwork, which generally contains a little moisture, may be advantageously coated with a paint that will enable it to "breathe" and thus avoid the formation of blisters, iron would appear to be best protected by an impermeable paint through which oxygen and water cannot pass.

Details of Experimental Method.

The method of experiment consisted essentially in exposing steel plates, coated with various paint mixtures and suspended on a specially constructed wooden fence, to the action of the weather for varying periods of time, and subsequently cleaning and noting the loss in weight due to corrosion.

The fence was erected on a low bank running almost due north and south, situated outside the city of Worcester in the valley of the Severn, some 200 yards from the river side. The author desires to thank the Worcester City Sewage and Waterworks Committee for allowing him free use of this ground.

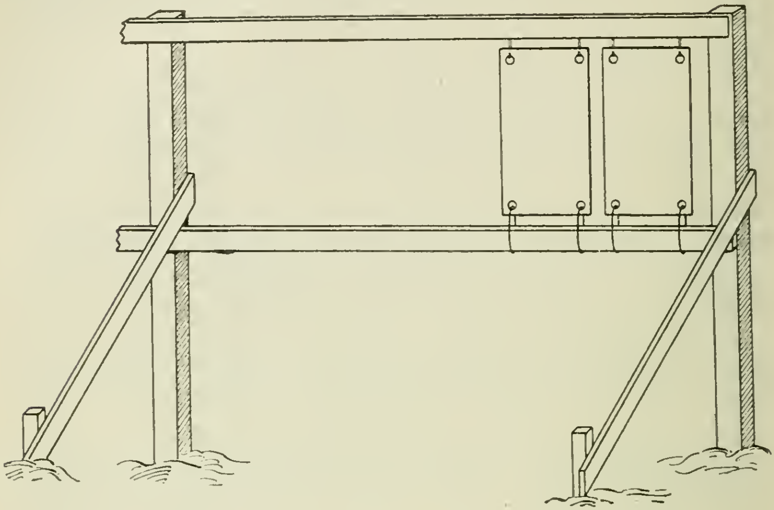

FIG. 1.

The fence measured some 90 yards in length, and was constructed as shown in Fig. 1. (See Plate V. and Fig. 1.)

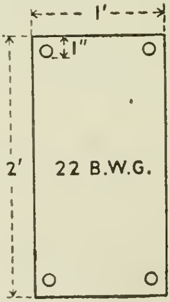

FIG. 2.

The plates were made of open-hearth steel, cold rolled and charcoal annealed. They measured 2 feet by 1 foot in area and 0·03 inch in thickness (No. 22, B.W.G.). A hole was punched near each corner to enable the plate to be firmly attached to the fence. The following analysis, made by Mr. J. Lloyd Bentley of Darlington, may be regarded as typical of all the plates, and is not very different from that of the Bessemer steel—one of the three grades of metal used in the Atlantic City tests.[1]

	Plates Used in this Research.	Atlantic City.
Carbon	0·11	0·08
Sulphur	0·04	0·05
Phosphorus	0·07	0·08
Manganese	0·35	0·35
Silicon	0·07	...

Each plate weighed approximately 2 lb. 4 oz., and was suspended by means of steel hooks to the upper cross bar of the fence, the other end being securely tied with copper wire to the lower cross bar. See Fig. 1.

Five plates were suspended between each two vertical posts. They were generally painted in one of three conditions, namely :

1. Exactly as they arrived from the mills, with the coating of scale upon them. The surfaces were very smooth, and enabled the paint to be applied with great evenness. Such plates are referred to as " scaled " in the sequel.

2. The scale was removed by sand-blasting. This gave them a rough surface which absorbed and gripped the paint extremely well.

3. The plates were first freed from oxide by immersion in dilute sulphuric acid contained in large leaden baths specially constructed for the purpose. They were then removed, washed, and allowed to soak in a solution of sodium hydroxide in order to effect the neutralisation of any acid remaining within the pores of the metal.[2] After an hour or two the plates were again thoroughly washed, dried between sheets of filter paper, and finally polished with emery paper. Plates treated in this manner are termed " pickled " in the sequel. Their surfaces were very smooth and did not grip the paint at all well, although the artistic effect as manifested by the even appearance of the painted surface was noteworthy.

This method of pickling is substantially the same as that employed in the Atlantic City tests. Walker[3] and Voorhees, on the other hand, do not approve of it, claiming that the traces of salts left behind add an unknown factor to the corrodibility of the plates and thus complicate the results. They therefore recommend the use of sand-blasted surfaces. Theoretically this is perfectly sound. In practice, however, it was found that the results obtained with pickled plates were quite as uniform as those with sand-blasted ones. It would appear, therefore, that if any disturbance actually occurs it is fairly uniform for all plates so treated.

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[1] Cushman and Gardner, *op. cit.*

[2] See Friend, *Transactions of the Chemical Society*, 1912, vol. ci. p. 50.

[3] Walker and Voorhees, *loc. cit.*

A few plates were for special reasons subjected to different treatments, but full details of these are given in the sequel. The various paint mixtures were prepared by thoroughly mixing together in an earthenware mortar the different ingredients in the requisite proportions. These consisted of dry pigment, oil, and occasionally turpentine or benzoline. The pigments were always dried in a steam-oven at 100° C. prior to weighing, for powders are remarkably hygroscopic and may contain anything up to 10 per cent. of moisture, and even higher, according to circumstances.

The oils used in this research were obtained from Messrs. Mander Brothers of Wolverhampton, several of them being specially prepared for the author by Dr. Morrell. They were as follows:

No. 1. Pure Calcutta raw linseed oil.

No. 2. Pure Baltic raw linseed oil.

No. 3. Oil No. 2, heated 30 hours at about 200° C. No drier.

No. 4. Oil No. 2, heated for 36 hours at about 300° C. No drier.

No. 5. Oil No. 2, heated for 42 hours at about 300° C. No drier.

No. 6. Oil No. 1, heated for 2 hours with PbO up to 150° C.

No. 7. Oil No. 1, heated for 16 hours to maximum temperature of 305° C. No drier.

No. 8. Oil No. 1, heated for 4 hours with ½ per cent. Cyprus umber up to 205° C.

No. 9. Oil No. 1, heated with 1½ per cent. of manganese hydroxide for 2 hours up to 150° C.

No. 10. Oil No. 1, heated with 1 per cent. of litharge for 4 hours up to 205° C.

No. 11. Oil No. 1, heated for 4 hours to 270° C. No drier.

In speaking of a paint it is convenient to express the proportion of pigment as a percentage. Thus, in the sequel, by "a 30 per cent. Venetian red paint" is understood a mixture containing 30 per cent. by weight of dried Venetian red pigment, the remaining 70 per cent. consisting of the liquid vehicle (linseed oil).

The paints prepared in the above manner were transferred to beakers, and weighed quantities applied by means of small brushes to the plates. The last named had already been tared and were laid in a horizontal position to prevent the paints from "running." When the paint had thoroughly set the plates were turned over so that their other sides might be treated in the same manner. When these second coats had set the plates were usually ready for exposure and were suspended, as already indicated, on the fence, the greatest care being taken during transit to avoid scratching or other mechanical injury.

At the close of the requisite interval, ranging from five months to two and a half years, according to circumstances, the plates were removed and soaked in a concentrated solution of sodium hydroxide in order to loosen the paint. After washing and drying the adherent rust was removed with emery paper and the plates again weighed. The difference in weight between the plates at this stage and when they were cleaned prior to painting some months previously represented the loss due to corrosion, and hence gave a quantitative indication of the protection afforded by the paint.

SOURCES OF ERROR AND THEIR AVOIDANCE.

The method of experiment detailed above is subject to several sources of error, the more serious of which may be discussed at this stage, together with the means adopted for minimising their effect.

1. *Irregularities in the Metal.*—It is commercially impossible to prepare series of steel plates perfectly homogeneous in character and identical in their physical conditions and chemical constitutions. Consequently two plates upon exposure to the same corroding media will not rust to exactly the same quantitative extent. This variation clearly limits the value of corrosion methods as applied to the determination of the relative protection afforded by different oils and paints.

For example, five plates used in this research were pickled and exposed on the fence, without any protective coat, to the action of the weather for one month. They were then removed, weighed, cleaned with emery paper, and weighed again. The difference in weight gave the amount lost as rust. The results for four of the plates were as follows:

	Loss in Weight. Grammes.
Plate 1	1·55
„ 2	1·25
„ 3	1·35
„ 4	1·60
Mean	1·44

The extreme plates show a variation of + 0·16 gramme (11 per cent.) and – 0·19 gramme (13 per cent.) from the mean. These results may be regarded as quite satisfactory for this kind of work.

The fifth plate, however, lost 3·95 grammes, or nearly three times the mean loss of the other plates. So great a variation can hardly be attributed to the method of experiment. It is almost certainly due to variation in the quality of the metal in the plate. The effect of this irregularity may, to a large extent, be overcome by treating not one plate merely, but several plates with the paint to be tested. In the present research five plates were usually employed in each test, and whilst the individual members of such series frequently exhibited considerable variation in corrodibility, the mean results were found to be fairly reliable for purposes of comparison.

2. *Variation in the Weather.*—Since the plates were exposed in the open air, the activity of which could not be controlled, it was necessary to expose and to subsequently take down on the same dates all those plates that were to be directly compared with one another.

3. *Positions of the exposed Plates.*—As has already been mentioned, the plates were painted in series of five, and were exposed on the fence in groups of the same number. Thus, for example, three such sets might be placed in numerical order as follows:

1, 2, 3, 4, 5   6, 7, 8, 9, 10   11, 12, 13, 14, 15

Owing to the protection afforded by the vertical posts to the left and right alternately of plates 1, 5, 6, 10, 11, and 15, these will not corrode at quite the same rates as the middle plates. The irregularity, however, is the same for each series, and the mean result for each set of five plates is in consequence strictly comparable with that of the other sets. In order to render the results still more reliable, the different series were intermixed in such a manner that the five plates in each series occupied each of the five possible positions, namely, two exterior and three interior, but in different sections of the fence.

4. *Application of the Paint.*—Whilst after a little practice it is not difficult to cover the surface of a steel plate with a uniform layer of paint, the task of applying in a similar manner a definitely weighed quantity of paint is much less simple. When an even coat of paint has been applied it is usually found that a trifle more or less of the requisite weight has been taken ; if the former, the excess must be taken up with the brush ; if the latter, a small addition must be made. It is these final operations which render the task of obtaining a perfectly uniform distribution extremely difficult.

Closely allied to this is the problem of applying a thoroughly representative sample of the paint to the plate. As a general rule, when five plates required treatment sufficient paint for several more was made up. On inserting the brush into the mixture a certain amount of oil is absorbed by the hairs and, whilst in thin paints[1] this is of no particular moment, in the case of the thicker paints containing relatively small quantities of oil, the ratio of oil to pigment may be unduly disturbed.

This difficulty was overcome by using small brushes, and such as had already been used for thinner paint composed of the same kind of pigment and oil. The hairs then contained sufficient oil and did not impoverish the thick paint. An even more serious source of error was found to lie in the tendency of the pigment to settle out of the paint. The denser pigments were particularly troublesome in this respect, and although every effort was made to stir thoroughly and maintain a uniform composition during application, the last coat of paint to be applied in any series was invariably a trifle thicker than the first. In order to neutralise the effect of this irregularity as far as might be, the plates were painted on one side in a definite order, which order was reversed when the other sides were treated.

5. *The Extent of Corrosion.*—It was found desirable not to allow corrosion to proceed too far before discontinuing the

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[1] That is, paints with high oil and low pigmentary contents.

experiments. When once the paint film had begun to disintegrate and the underlying metal to rust, further corrosion proceeded rapidly and almost independently of the kind of paint originally applied. Consequently the most reliable indications of the efficiency of the paint were obtainable before this stage of excessive corrosion had been reached.

6. Mention has already been made of the difficulty of determining small differences in weight of heavy plates (see p. 81). In the Atlantic City tests, and in those by Walker and Voorhees, no weighings were made, the efficiency of the paint being judged from the appearance after prolonged exposure. Consequently in those researches this difficulty did not arise, and plates $\frac{1}{8}$ inch in thickness were employed. In order to reduce the weight of the plates per unit area in the present research, the thickness averaged only 0·03 inch. Even then, however, the plates weighed approximately 2 lb. 4 oz. or 1000 grammes, and a loss in weight of 1 gramme thus only represents 0·1 per cent. Owing to the absence of the author from home on military service, it has been impossible to always use the same weights for the final weighings of the plates as for the initial. Consequently the absolute losses in weight of the plates are not always correct, although the relative losses are quite reliable, inasmuch as all the plates to be compared with one another were weighed at the same time with one set of weights initially, and again at the same time and with another set of weights at the conclusion of the tests, the same error being thereby rendered constant throughout. This explains the apparent gain in weight of the plates in Series II., XXXVII., and XXXVIII.

The foregoing considerations will serve to emphasise the necessity of making a considerable number of tests before drawing any definite conclusions. They also indicate that the mean loss in weight obtained for any particular series of five plates is probably, for purposes of comparison, a fairly accurate figure, even although the individual results in such a series vary amongst themselves.

The Relative Proportions of Oil and Pigment.

The influence of varying the relative proportions of oil and pigment upon the protective properties of paint appeared worthy of careful study. The problem may be attacked in three ways, namely :

A. *Employing the same Weight of Pigment.*—In Series XXVI. and XXXII. the same weight of French ochre, namely, 4·5 grammes, was applied to each side of each plate, but the weight of linseed oil ranged from 4·5 grammes in Series XXVI. to 6·3 grammes in Series XXXII.

Series.	No. of Plates.	Composition of Paint by Weight.	Grammes of Paint on each Side.	Grammes of Oil on each Side.	Length of Exposure. (Months.)	Mean Loss in Weight. (Grammes.)
XXVI.	169–173	50 ochre 50 oil No. 8	9·0	4·5	20	2·24
XXXII.	199–203	50 ochre 70 oil No. 8	10·8	6·3	20	1·83

As was, perhaps, to be anticipated, an increase in the weight of oil applied to the surface of the metal led to a decided decrease in corrosion.

B. *Employing the same Weight of Oil.*—In the following series the same weight of oil, namely, 4·5 grammes, was added to each

Series.	No. of Plates.	Composition of Paint by Weight.	Grammes of Paint on each Side.	Grammes of Pigment on each Side.	Relative Mean Loss in Weight.
XXIII.	154–158	Oil No. 8	4·5	...	Rapidly destroyed
XXVII.	174–178	30 D.I.R.[1] 70 oil	6·43	1·93	100
XXX.	189–193	40 D.I.R. 60 oil	7·5	3·0	39
XXIV.	159–163	50 D.I.R. 50 oil	9·0	4·5	39
XXIX.	184–188	60 D.I.R. 40 oil	11·25	6·75	30
XXXIX.	234–235	80 D.I.R. 20 oil	33·0	28·5	95
XXXIII.	204–208	30 red lead 70 oil No. 1	6·43	1·93	100
XXXIV.	209–213	40 R.L. 60 oil	7·50	3·0	60
XXXV.	214–218	50 R.L. 50 oil	9·0	4·5	58
XXXVI.	219–223	60 R.L. 40 oil	11·25	6·75	21
XXXVII.	224–228	70 R.L. 30 oil	15·0	10·5	19
XXXVIII.	229–233	80 R.L. 20 oil	22·5	16·0	0

[1] Deep Indian red pigment.

side of each plate, but with varying amounts of pigment. The plates were exposed to the air for 29 months.

These results are shown diagrammatically in Fig. 3.

It will be observed that, in the case of the experiments with deep Indian red, the first few additions of pigment led to a marked increase in the protective power of the paint, a maximum being reached with 60 per cent. of pigment. This mixture worked very satisfactorily under the brush and yielded a good coat. On increasing the percentage of pigment to 80, the paint became too thick to work without a diluent, and sufficient benzoline was therefore added to facilitate the application of an even coat to the plate. As the benzoline evaporated completely on standing, leaving no residue, the proportion of liquid vehicle to pigment ultimately remaining on the plate was in no wise altered by its use. The steel soon corroded, however, under this 80 per cent. paint.

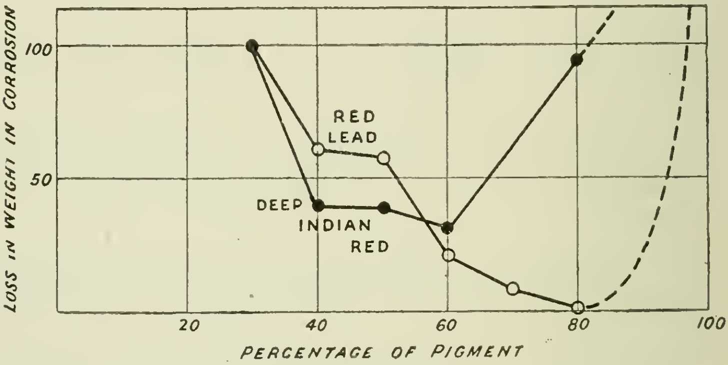

Fig. 3.

In the case of the red-lead experiments, however, the best protection was afforded by the 80 per cent. mixture. This worked rather stiffly under the brush but could, nevertheless, be easily applied as a uniform coat without the addition of any thinner. Since red lead alone, without a liquid vehicle, could not protect iron owing to its lack of adhesion, it is evident that the maximum protection would be afforded by some concentration of pigment intermediate between 80 and 100 per cent. This is an exceptionally important observation, inasmuch as it proves that different oils and pigments have different optimum proportions in which they exert their maximum protective effects.

Analogous results are obtained by :

C. *Employing the same weight of paint,* but varying the relative proportions of pigment and oil. This is evident from a consideration of the following series, the weight of paint on each side of the plates amounting to 9 grammes :

Series.	No. of Plates.	Composition of Paint by Weight.	Weight of Pigment on each Side. (Grammes.)	Weight of Oil on each Side. (Grammes.)	Length of Exposure. (Months.)	Mean Loss in Weight. (Grammes.)
XXI.	144–148	30 V. red 70 oil No. 6.	2·7	6·3	5	1·12
XIII.	104–108	50 V. red 50 oil	4·5	4·5	5	3·82
XVI.	119–123	60 V. red 40 oil	5·4	3·6	5	15·03
XXII.	149–153	30 V. red 70 oil No. 6.	2·7	6·3	7	0·93
XIV.	109–113	50 V. red 50 oil	4·5	4·5	7	7·94
XVII.	124–128	60 V. red 40 oil	5·4	3·6	7	20·66

These results are shown graphically in Fig. 4, and are of increased practical interest inasmuch as it is customary to compare the protective values of equal weights of paint rather than of equal weights of any one of the constituents of the same.

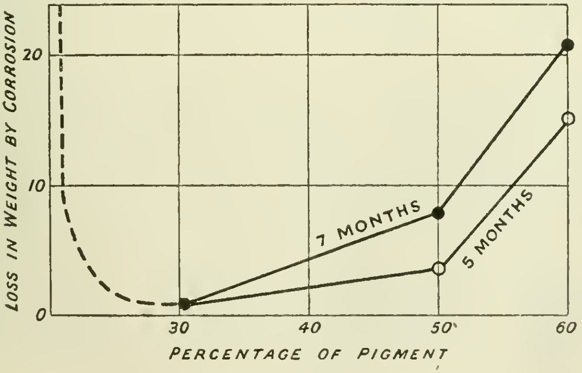

FIG. 4.

It is abundantly evident that, *where equal weights of paint are to be applied*, the greatest protection is afforded by a paint containing a high proportion of good oil. After five months' exposure the plates covered with 60 per cent. Venetian red paint lost fourteen times as much by corrosion as those with 30 per cent. paint, whilst in the experiments of seven months' duration the former had lost nearly twenty-one times as much.

The shape of the curves indicates that a further reduction in the percentage of pigment below 30 could hardly be expected to yield a paint of higher efficiency; in fact, owing to loss of "body" and of hardness the paint would probably be considerably less efficient. With no pigment and 100 per cent. oil very poor protection is afforded, as was demonstrated in § B above. This is indicated in the figure by the broken line.

From the foregoing data it would appear that with the particular oil and pigment under discussion the optimum proportion of the latter is about 30 per cent. for the experimental conditions described.

Different pigments may well be expected to yield different optimum concentrations under these conditions, just as was found to be the case in § B above. For this there are probably several contributory causes, which may be summarised as follows:

1. *Chemical.*—It was observed that the red lead paint used in Series XXXIII. to XXXVIII. gradually became less opaque as the length of exposure increased. After two years the 40 per cent. paint (Series XXXIV.) became quite colourless, the plates presenting the appearance of having been painted simply with raw oil without any pigment. Series XXXIII., containing 30 per cent. of red lead, had already been colourless for several months; Series XXXV., containing 50 per cent. of red lead, was nearly colourless, whilst the 60 per cent. paint (Series XXXVI.) had also suffered considerable loss of opacity. This observation is interesting in view of the results obtained by Gardner on leaving pigments finely ground in oil for two years in air-tight vessels.[1]

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[1] Gardner, *Journal of the Franklin Institute*, 1912, vol. clxxiv. p. 415. *Journal of Industrial and Engineering Chemistry*, 1911, vol. iii. p. 628. See also Boughton, *U.S. Department of Agriculture, Bureau of Chemistry*, Circular No. III., 1913.

The oil was removed and its ash determined, with the following results :

	Ash. Per Cent.
Pure oil	0·19
Carbon black	0·195
Iron oxide	0·456
Red lead	15 56

Clearly red lead combines with linseed oil, whether the latter is the unoxidised liquid or oxidised to solid linoxyn. Chemical activity of this kind cannot fail to influence the optimum concentration of pigment for protective purposes.

2. *Physical.*—A consideration of the physical properties of pigments, quite apart from any chemical activities they may possess, indicates very clearly that two pigments cannot be expected to have the same optimum concentrations. For example, some pigments, such as lampblack, are very "hungry" and require to be mixed with a large amount of oil in order to yield a sufficiently thin and easily workable paint. Others, like red lead and zinc oxide, are the reverse. This is well illustrated by the following data, obtained by adding raw linseed oil to a given weight of pigment (about 10 to 20 grammes) in just sufficient quantity to enable the mass to adhere as a stiff putty.

Pigment. (100 Grammes.)	Specific Gravity.[1]	Oil required. (Grammes.)
Lampblack	0·517	40
Ochre	2·42	32
Indian red	2·038	21
Red lead	7·02	7

From the results in § B with red lead and Indian red it is evident that the greater the "hunger" of the pigment the less is the percentage required to yield the most efficient protective paint. It is also instructive to note that the hunger does not always fall with rise of specific gravity of the pigment. Ochre and Indian red are cases in point.

The foregoing results have a most important bearing upon tests carried out with different pigments with a view to determining which is most suitable for the protection of iron.

It is easy to see that three pigments, A, B, and C, might be chosen possessing different optimum concentrations, as indicated in Fig. 5. If, now, different plates of iron were painted with, say, equal weights of mixtures containing 25 per cent. of pigment and 75 per cent. of oil, the best result would be obtained with pigment A and the poorest with C. Had, however, a 50 per cent. paint been taken, B would have yielded the highest protection, whilst with 80 per cent. of pigment the first positions are entirely reversed, C giving the best result and A the worst.

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[1] Determined by Mr. J. Lloyd Bentley of Darlington.

This is a point deserving very careful consideration, as it probably affects all experiments that have as yet been carried out with the object of determining the most suitable pigments for protective purposes; and there can be little doubt that herein lies an explanation for many of the apparently contradictory results that have been obtained. Correctly speaking, the real comparative efficiencies of pigments can only be obtained by comparing them when used in their optimum concentrations.

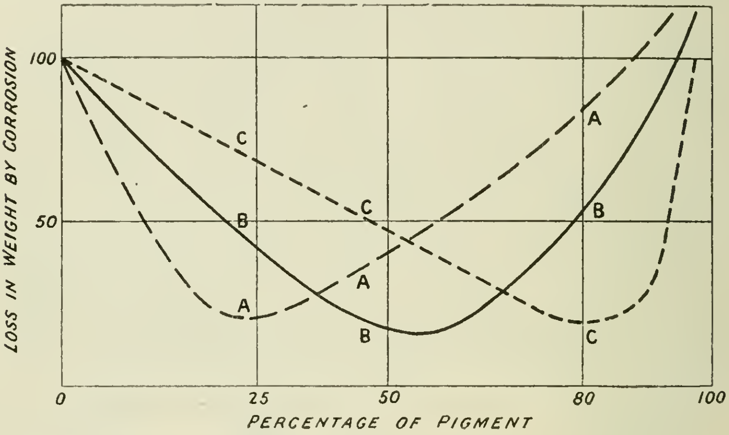

Fig. 5.

To determine the optimum concentrations for all the different kinds of pigment on the market would be a very long and arduous process. Fortunately the curves in Figs. 3 and 4 are fairly flat in the region of these optima, suggesting that considerable latitude in the percentage of pigment may be allowed to meet other desirable properties of the paint without seriously affecting its protective power.

In this connection it is interesting to recall the results obtained by Dubois,[1] who exposed plates of iron painted with linseed oil and varying quantities of kauri varnish to the action of oxygen and corroding gases, kept moist with steam. It was observed that addition of the kauri varnish to the linseed oil up to 20 per cent. enhanced its protective power in proportion to the amount of varnish added : 20 per cent., however, constituted the optimum concentration, further addition diminishing the efficiency of the mixture.

Conclusion.—The foregoing considerations indicate that :

1. The best results may be expected from paints possessing as high a percentage of oil as is compatible with good body and with any other working properties that have to be considered for the particular purpose in hand.

2. The greater the hunger manifested by the pigment the lower is the percentage of it required in the paint.

Linseed Oil as a Vehicle.

Pigments cannot by themselves constitute a paint or protect iron from corrosion ; a binding medium or vehicle is essential. To this end linseed is chiefly employed, because upon exposure to air it oxidises to a tough, elastic substance known as linoxyn. The chemical and physical changes involved in this process merit careful study.

When spread in thin layers upon some non-absorbent material such as glass, linseed oil absorbs oxygen from the air, thereby increasing in weight, in density, and also in volume.

At first there is a period of induction, during which no appreciable alteration takes place. This is followed in the course of a day or two by a relatively rapid rise in weight to a maximum, after which a slow but fairly steady loss ensues, owing to a gradual decomposition of the oil film consequent upon continued slow oxidation. The maximum increase in weight varies both with the oil and the conditions of experiment, the most reliable of published data ranging from 13 per cent.[2] to 25·6 per cent.[3] The average figure, however, is about 18 per cent. at

[1] Dubois, *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. p. 968.

[2] Redman, Weith, and Brock, *ibid.*, 1913, vol. v. p. 630.

[3] Ingle, *Journal of the Society of Chemical Industry*, 1913, vol. xxxii. p. 639.

ordinary temperatures. The oil now slowly decreases in weight. The existence of a maximum increase in weight does not mean that oxygen now ceases to be absorbed. On the contrary, oxygen is taken up continuously by the oil film, which steadily increases in density and hardness. The explanation is that, during the initial stages of oxidation of the oil, volatile products are continuously evolved, at first in small amounts, and gradually more rapidly, until ultimately their weight equals and finally exceeds the rate of oxygen absorption. The point of maximum increase in weight is thus the stage at which the weight of oxygen absorbed exactly equals that of the products evolved. The oil is then a tough, elastic, and transparent solid. If oxidation were to cease at this point the film would be very permanent and constitute an ideal binding agent for the pigment. Unfortunately, however, oxidation continues, the linoxyn evolving water, carbon dioxide, formaldehyde, &c., and becoming simultaneously lighter but denser.

Although it has long been known that the initial increase in weight is accompanied by an increase in volume, only one attempt appears to have been made to determine what the extent of this latter may be.[1] The results were as follows ; raw Calcutta oil, No. 1, p. 86, being employed :

Condition of Oil Raw, No. 1.	Percentage Increase in Weight.	Density at 15° C.	Percentage Increase in Volume.
Liquid	...	0·93179	...
,,	2·08	0·94850	0·28
,,	5·83	0·97696	0·87
Thick, frothy liquid	9·66	1·00123	2·06
Tacky	14·14	1·0424	2·0
Just set	17·34	1·0582	3·3
Solid linoxyn	17·90	1·0656	3·1
,,	18·57	1·0902	1·35
,, (3 months old)	10·3	1·1054	− 7

From the foregoing it is evident that the oil reached a maximum increase in volume of 3·3 per cent. shortly before its maximum weight was arrived at. The density of the oil steadily increased, becoming slightly greater than that of water with a 10 per cent. rise in weight, although it was still in the liquid condition.

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[1] Friend, *Transactions of the Chemical Society*, 1917, vol. cxi. p. 162. Also "The Chemistry of Linseed Oil" (Gurney and Jackson, 1917).

It will also be observed that the oil became increasingly viscous. Hence when a coating of oil is applied to a non-absorbent surface the outermost layers, which are the first to oxidise, increase both in volume and viscosity, thereby tending to cause crinkling. This may, of course, be overcome by the application of very thin coats of oil. The oil films on each of the plates in Series XXIII. crinkled slightly, and that no doubt materially weakened the protective power, the metal beneath the troughs of the crinkles rapidly corroding. It will be evident that the increase in volume is a function of the increase in weight. Hence any factor tending to reduce the latter must also reduce the expansion. Sabin [1] and Gardner [2] have shown that the addition of various pigments to linseed oil effects a reduction in the maximum increase in weight of the oil, even when those pigments are chemically inert, like barytes and silica. Probably this is due to a physical catalytic acceleration of the decomposition of the oil. Whatever the cause, the result is the same. Consequently it is difficult to calculate the amount of expansion to be expected in any particular case.

Oil that had been exposed to the air for three months showed an increase in weight of 10·3 per cent., but a contraction in volume of 7 per cent. After further prolonged exposure the contraction becomes proportionately greater. Thus Sabin [3] mentions a case where a film of oil exposed to the air for eight months showed only a gain in weight of about 2 per cent., its density being 1·098. The original density of the oil is not given, but assuming it to have the mean value of 0·932, it is easy to calculate that the total shrinkage must have been 13·4 per cent.

It seems quite unnecessary, therefore, to explain the cracking of old paint surfaces on the assumption of electrical action exerted by the pigments suspended in the linoxyn, as does Täuber.[4] The most obvious explanation is that the linoxyn cannot continue to contract indefinitely without rifts appearing to ease the surface strain.

[1] Sabin, *Journal of Industrial and Engineering Chemistry*, 1911, vol. iii. p. 84.

[2] Gardner, *ibid.*, 1914, vol. vi. p. 91.

[3] Sabin, *loc. cit.*

[4] Täuber, *Chemiker Zeitung*, 1909, vol. xxxiii. pp. 85, 94.

The Porosity of Linoxyn.

If linoxyn were perfectly impervious to moisture then a film of paint containing it would preserve iron from corrosion so long as the linoxyn remained free from mechanical injury or from cracks resulting, as explained in the previous section, from prolonged oxidation and consequent shrinking.

Unfortunately, however, linoxyn is porous to moisture, and the problem arises as to whether or not it is possible to so treat linseed oil that upon oxidation the resulting film shall have the minimum porosity.

When heated in the absence of air linseed oil polymerises and thickens. This is well illustrated by the following data:[1]

	Density at 15° C.	Relative Viscosity.	Molecular Weight.
Oil No. 2. Raw Baltic	0·9337	100	740
Oil No. 3. Same oil heated 30 hours at 200° C.	0·9325	73	760
Oil No. 4. Same oil heated 36 hours at 300° C.	0·9476	459	1000
Oil No. 5. Same oil heated 42 hours at 300° C.	0·9626	3770	1420

Polymerisation clearly takes place at temperatures as low as 200° C.

The porosity of linoxyn from these oils to water vapour was now determined. Several methods of doing this have been described,[2] but the present author regards the method previously adopted by him as most simple and very efficient,[3] since accurate duplicate results are obtainable. The method consists in saturating filter papers with the oil, allowing to set by prolonged exposure to air, and tying them over the mouths of small flasks containing lumps of calcium chloride. The flasks are now placed, together with a dish of water, under a large bell-jar, and the increase in weight, due to absorption of water vapour by the calcium chloride, is regularly determined.

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[1] Friend, *Transactions of the Chemical Society*, 1917, vol. iii. p. 162.

[2] Perry's method, as described by J. C. Smith, *Journal of the Iron and Steel Institute*, 1909, No. I. p. 91. See Cushman and Gardner, *op. cit.*; Muckenfuss, *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. p. 535.

[3] Friend, *Carnegie Scholarship Memoirs*, 1911, vol. iii.

The results were as follows :

Oil.	Increase in Weight after 28 Days. (Grammes.)	Relative Permeability.	Molecular Weight.
No. 2 (raw) . .	3·30	100	740
No. 3 (heated) .	3·45	105	760
No. 4 (,,) .	2·60	79	1000
No. 5 (,,) .	1·16	35	1420

The decrease in permeability with rise of molecular weight is very striking.

It seemed useful to determine the relative efficiencies of paints made with these oils, and field tests were accordingly set up with the following results :

Duration of tests . . . . $2\frac{1}{2}$ years
Weight of paint on each side . . . . . 12 grammes

Series.	No of Plates.	Composition of Paint by Weight.	Mean Loss in Weight due to Corrosion.	Relative Corrosion.
XLVII.	271–275	45 Venetian red 55 raw oil No. 2	1·32	100
XLVIII.	276–280	45 V. red 55 oil No. 3	2·06	156
XLIX.	281–285	45 V. red 55 oil No. 4	0·74	56
L.	286–290	45 V. red 55 oil No. 5	0·41	31

The foregoing results illustrate the superiority of polymerised oils.

THE FUNCTIONS OF A PIGMENT.

Linseed oil alone, as indicated by the results of Series XXIII., p. 91, does not afford an efficient protective coating for iron. Addition of a suitable pigment greatly enhances its value for many reasons, the chief of which may be summarised as follows :

1. The pigment offers mechanical support to the linoxyn, thereby affording a harder and tougher film, which is proportionately resistant to mechanical injury.

2. The pigment, being itself impervious to moisture, reduces the permeability of the paint film. By suitably blending the sizes of the pigmentary particles and thoroughly incorporating

them with the oil, a paint is obtained capable of offering a high resistance to water, whether liquid or vapour.

3. The same property also renders the paint less permeable to oxygen. Consequently the oil itself is preserved from rapid oxidation and deterioration.

4. The paint is more viscous than the free oil. It can be applied in a thicker coating without "running."

5. The addition of pigment to the oil reduces the amount of expansion of the oil on setting, so that the tendency to crinkle is greatly reduced, and thicker coats may safely be applied. All the plates coated with oil alone in Series XXIII. showed signs of crinkling, and this tended to assist the corrosion of the underlying metal.

THE RELATIVE VALUES OF THIN AND THICK COATS OF PAINT.

The protection afforded by applying thin and thick coats of paint respectively to iron plates has been studied, and the results are given in the accompanying table:

Series.	No. of Plates.	Composition of Paint by Weight.	Grammes of Paint on each Side.	Length of Exposure. (Months.)	Mean Loss in Weight. (Grammes.)
VI.	26–30	100 Venetian red	7	21	3·83
VII.	31–35	50 turpentine	10·5	21	1·78
VIII.	36–40	200 oil No. 7	17	21	1·41
XIII.	104–108	50 Venetian red	9·0	5	3·82
XVIII.	129–133	50 oil No. 6	14·0	5	1·07
XIV.	109–113	,, ,,	9·0	7	7·94
XIX.	134–138	,, ,,	14·0	7	2·00
XXIV.	159–163	50 deep Indian red	9	29	3·04
XXVIII.	179–183	50 oil No. 8	16	29	1·49

From the foregoing data it is evident that, unless the thickness of the paint is excessive, the thicker the coat the greater is the protection it affords to the underlying metal. In every case, however, there is an optimum weight of paint that can be applied in any one coat, and if that amount is exceeded the efficiency of the paint is reduced. What that optimum thickness may be depends, in the main, upon the tendencies of the paint to "run" and crinkle. These tendencies are influenced by several factors, chief amongst which are :

1. *The Nature of the Oil.*—Linseed oil varies considerably in viscosity according to its treatment (see p. 100). Litho or polymerised oils may be prepared as very thick liquids, and as the viscosity rises so does the tendency to run become less. Paints prepared from these may therefore be applied more thickly, other things being equal, although crinkling due to the expansion of the oil on setting has still to be guarded against.

2. *The Relative Proportions of Oil and Pigment.*—For example, a paint consisting of 10 per cent. Indian red and 90 per cent. raw linseed oil will readily run and crinkle if applied thickly to a non-absorbent surface such as iron. A very thick coat of 80 per cent. Indian red and 20 per cent. raw oil may, on the other hand, be applied without danger either of running or of crinkling, for the simple reason that the high proportion of pigment stiffens the paint and renders any flowing movement proportionately difficult.

3. *The Proportion and Volatile Character of the Thinner.*—A paint containing a high proportion of volatile thinner, such as benzoline, may frequently be applied, particularly to horizontal surfaces, more lavishly than its low viscosity would indicate, because the thinner rapidly evaporates, leaving a stiffer but thinner coat of paint to set at leisure.

4. *The Shape and Position* of articles to be painted exert their influence. Horizontal plates as used in the present research obviously show less tendency to run than vertical plates or bars.

Evidently, therefore, it is impossible to say what is the optimum weight of paint that may be efficiently applied in a single coat unless the conditions of painting are exactly known. It may be stated, however, that in general, provided neither running nor crinkling of the paint surface takes place before or during setting, the optimum thickness has not been exceeded.

Advantage of Multiple Coats.

Closely allied to the previous problem, namely, that of determining the influence of increasing the thickness of the coat of paint, is that of multiple coats.

Liebreich[1] and Spitzer found, as the result of experiments, by a method already described in this memoir and adversely criticised, that by increasing the number of coats the tendency of the underlying metal to corrode was enhanced. Four coats of paint gave distinctly less favourable results than a single thin coat. Arndt[2] has taken exception to these results and suggests, by way of explanation, that the highly polished surfaces of the experimental plates used by Liebreich and Spitzer were unsuitable for the purpose, owing to the lack of grip afforded to the paint. Addition of a second, third, and fourth coat to the first one, therefore, tended to draw the last named away from the metal. Moisture and air collected in the space thus formed, with the result that corrosion was accelerated. Arndt suggested further that the experiments might with advantage be repeated, using iron plates with roughened surfaces such as a sand-blast yields. Liebreich[3] and Spitzer accepted the suggestion, repeated their experiments with sand-blasted iron, and obtained the same results. They do not, therefore, accept Arndt's hypothesis, but explain their results on electro-chemical grounds, according to which the boundary between the iron and its coat of paint contains hollows and hillocks of almost microscopic size in the case of highly polished metal plates. These hollows become filled with water, due either to decomposition of the linseed oil, which is well known to evolve water when setting, or to direct absorption of moisture from the atmosphere. This water serves to connect electrically the metallic iron and pigment, the former becoming anodic and the latter the cathode. The iron thus readily oxidises. Mathematical arguments are adduced to show that the thicker the coat of paint the greater is the potential difference between the metal and pigment, and hence the greater tendency of the iron to rust.

The arguments are distinctly plausible, and appear to offer a satisfactory explanation for the results obtained by the authors under the particular conditions of their experiments. Not content with this, however, Liebreich and Spitzer, without any further experimental justification, state that without doubt (*zweifelsohne*) it may be regarded as a general axiom (*ganz*

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[1] Liebreich and Spitzer, *Zeitsch. Elektrochem.*, 1912, vol. xviii. p. 94.

[2] Arndt, *ibid.*, 1912, vol. xviii. p. 233.

[3] Liebreich and Spitzer, *ibid.*, 1913, vol. xix. p. 295.

allgemein gültig) that corrosion increases with the number of coats of paint. The German words are enclosed in brackets to show how emphatic the authors are in their conclusions.

The present author, however, does not regard acceleration tests as very valuable, and particularly deprecates the drawing from them of such important and far-reaching generalisations. The problem therefore appeared worthy of careful investigation.

In the accompanying table are detailed the results obtained with plates painted with 50 per cent. deep Indian red in oil No. 8, and exposed to the air for nearly two and a half years. (1) With one thin coat of 9 grammes on each side; (2) with one thick coat of 16 grammes on each side; and (3) with two thin coats on each side, namely, 9 and 7 grammes respectively.

Series.	No. of Plates.	No. of Coats.	Total Weight of Paint each Side. (Grammes.)	Length of Exposure. (Months.)	Mean Loss in Weight. (Grammes.)
XXIV.	159–163	1	9	29	3·04
XXVIII.	179–183	1	16	29	1·49
XXV.	164–168	2	16	29	1·02

From the foregoing it is abundantly evident that under the conditions of the experiments not only do two coats protect the metal from corrosion more efficiently than one thinner coat, but even slightly more efficiently than one thick coat containing the same weight of paint.

These results are in harmony with those obtained by Walker[1] and Voorhees in a somewhat different manner. Fifteen different paint mixtures were experimented with, being applied in one, two, and three coats, respectively, to large steel plates and exposed in tanks to alternate wet and dry. It was invariably found that the greater the number of coats the more perfect the preservation of the metal. Whilst, therefore, under the particular conditions described by Liebreich and Spitzer an increase in the number of coats of paint appears to have enhanced the corrosion, the conclusion of these authors that the same result will apply universally is quite incorrect. The unreliability of acceleration tests is thus convincingly emphasised. It is clear that when information of this kind is required the experiments should be carried out under conditions approximating as closely as possible to those to which the materials will be subjected in practice.

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[1] Walker and Voorhees, *Journal of Industrial and Engineering Chemistry*, 1913, vol. v. p. 899.

The foregoing results are of practical interest for another reason. In 1913 were published[1] the results of immersing iron plates for prolonged periods in water, the plates having been previously painted in various ways. The results seemed to indicate that the thicker the coat of paint the greater the tendency to corrode, precisely as in Liebreich and Spitzer's experiments. They were as follows:

	Grammes.
Mean loss of two plates, each coated with 4 grammes of rouge paint on each side	3·69
Loss of plate coated with 2 grammes of similar paint on each side	3·10

These results, if confirmed by later experiments which the author has in view, will be of particular interest to marine engineers as illustrating an important difference between paints suitable for aerial structures and those for subaqueous.

In this connection it is useful to draw attention to Walker's[2] observation that lacquered fruit-cans corroded more rapidly than unlacquered ones. The cans had been coated with a high-grade copal linseed oil varnish which appears to have acted as a depolariser, absorbing the protective film of hydrogen produced by the action of the acid fruit liquors upon the metal, thus exposing the latter to repeated attack and thereby hastening its corrosion.

Clearly each type of condition requires separate experimental investigation. No useful purpose can be served by drawing sweeping generalisations from the results of a few experiments.

THINNERS.

Thinners are added to a paint to reduce its viscosity, and thus to enable it to flow more easily under the brush. They also assist in the drying usually, as in the case of paraffin derivatives like benzoline, by enabling the paint to be spread in thinner layers, since the volatile thinner readily evaporates off; and also, as in the case of turpentine, by chemically assisting the oil to take up oxygen.

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[1] Friend, *Carnegie Scholarship Memoirs*, 1913, vol. v.

[2] Walker and Lewis, *Journal of Industrial and Engineering Chemistry*, 1909, vol. i. p. 754.

Thinners, such as benzoline, which evaporate completely without residue, cannot be expected to affect the properties of the paint after application. It was of interest to determine whether or not the addition of turpentine to a paint increases its efficiency, provided the same weight of original paint is applied. The results were as follows:

Length of exposure . . . . . . 20 months.

Series.	No. of Plates.	Composition of Paint by Weight.	Grammes of Paint on each Side.	Mean Loss in Weight due to Corrosion.
XXVI.	169–173	50 ochre 50 oil No. 8	9·0	2·24
XXXI.	194–198	50 ochre 50 oil No. 8 20 turps	10·8 (*i.e.* 9 grammes of original paint and 1·8 of turps)	2·11
XXXII.	199–203	50 ochre 50 oil No. 8 20 oil No. 8	10·8	1·83

These results are interesting as showing that the addition of turpentine to paint does very slightly enhance its efficiency provided, after evaporation of the turpentine, the same weight of original paint remains as is used for comparison. Clearly, however, it is more efficient to dilute or thin with oil, provided again a proportionately greater weight is added (Series XXXII.). Ordinarily, however, a thinner is added to increase the spreading power of the paint, and this reduces its thickness and hence its efficiency as a protective coating, as shown in the previous section.

INFLUENCE OF LIGHT AND COLOUR ON THE PERMANENCE OF PAINT.

It is a matter of common knowledge that light tends to accelerate many chemical reactions. The oxidation of linseed oil is no exception to this, and paints exposed to sunlight or diffused daylight set more rapidly than in the dark, other things being equal. It is not the light itself which effects the setting of the oil, for the latter when hermetically sealed in glass tubes appears unaffected by exposure to even the brightest sunlight. But in some obscure way light assists the oil to absorb oxygen, and thereby to harden, set, or dry. All kinds of light do not act with equal vigour, however. Cloez was apparently the first to prove this. By employing coloured glasses he was able to show that white light is most active, whilst red light is least so. From this it seems reasonable to infer that it is mainly the short waves that stimulate the oxidation of oil ; and this is supported by Genthe's observation that light emitted by a mercury lamp is particularly active in assisting raw linseed oil to set, such light consisting essentially of short waves.[1]

Since the disintegration of paint on prolonged exposure to air is also a process of oxidation, it seems reasonable to infer that the rate at which it takes place will likewise be affected by the kind of light to which paint is exposed. The paint might thus be expected to last longer in red light or in a shady place than when exposed to bright sunlight. Practical experience confirms this in so far as shade and sunlight are concerned.

The following experimental results are not without interest in this connection. Thin films of linseed oil No. 4 were spread on plates of coloured glass measuring 3¼ inches square, weighed and allowed to set, shielded from dust in a horizontal position. After the maximum increase in weight had been reached the plates were placed in a frame and fastened on the inner side of a window, the oiled side remote from the panes, so that the sunlight streaming into the room passed in succession through the window pane and coloured glass before reaching the oil.

The results were as follows :

Time. (Days.)	Colourless.		Red.		Yellow.		Green.		Blue.	
	Weight. (Grammes.)	Gain per Cent.	Weight. (Grammes.)	Gain per Cent.	Weight. (Grammes.)	Gain per Cent.	Weight. (Grammes.)	Gain per Cent.	Weight. (Grammes.)	Gain per Cent.
0	0·1524	...	0·1593	...	0·1558	...	0·1582	...	0·1577	...
24–27	0·1748	14·7	0·1818	14·1	0·1776	14·0	0·1799	13·8	0·1804	14·4
396	0·1610	5·7	0·1773	11·3	0·1724	10·7	0·1744	10·3	0·1652	4·7
571	0·1610	5·7	0·1783	11·9	0·1758	12·8	0·1738	9·9	0·1652	4·7

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[1] Genthe, *Zeitsch. angewand. Chem.*, 1906, vol. xix. p. 2087.

As usual the oil on each plate increased in weight to a maximum, arriving at that point after about twenty-seven days. As the plates were kept horizontal and in a shaded place for thirty days, the different colours had no opportunity of exerting their influence at this stage and the various maxima are seen to agree fairly closely.

The rate of subsequent decomposition proceeds much more slowly. Owing to the absence of the author on military service the experiments had to be discontinued after eighteen months; nevertheless the results, although admittedly incomplete, are not without value. The oil exposed on the colourless and blue plates loses in weight most rapidly, and that on the red and yellow plates disintegrates very appreciably more slowly. As might be expected, green lies nearly midway between the two extremes. Clearly, the shorter the waves of light the greater is the induced loss by oxidation.

By the employment of coloured pigments a similar effect might be expected to that obtained with coloured glasses. The problem, however, is not so easily attacked experimentally, for unless special precautions are taken, the results are liable to be marked by differences in the chemical or other physical actions of the pigments employed upon the oil. Thus, for example, white lead is a rapidly drying pigment, whilst lampblack is very slow; but this is not simply due to the fact that lampblack absorbs all light falling on to it, thereby preventing its accelerating the drying of the oil, whilst the white lead reflects the light and thus assists the oil to dry. Other important factors are concerned. In the case of black oxide of manganese and barytes the position is completely reversed, the black oxide, despite its blackness, being the better drier.

It was ultimately decided to attack the problem in two ways:

1. *Experiments with Wooden Panels.*—Four lake-pigments, namely, red, yellow, blue, and black, were specially prepared for the author by Messrs. Holmes of Newcastle, by adding the requisite dyes to barytes or barium sulphate. It was thought that by this means the pigments would have an identical chemical composition, save for the traces of the different dyes, coupled with similar physical properties, with the single exception of colour.

Wooden panels were painted with several coats of paint composed of 30 parts of linseed oil No. 8 intimately mixed with 70 parts of pigment. When these coats had thoroughly set the panels received a final coat of hard outdoor varnish. Several days later the panels were exposed to the weather on the fence already described.

After sixteen months the painted surfaces were carefully examined and photographed. The red and the black [1] showed weak cracks, whilst the yellow and the blue were much more seriously cracked. This is well illustrated in the case of the red and yellow panels in Plate VI. The results clearly support the author's contention.

2. *Experiments with Steel Plates.*—These were carried out with the same lake-pigments as the previous experiments, the white " lake " consisting of pure barytes without any dye. Each plate received two coats of paint on either side, the whole set being exposed to the weather for twenty-seven months. The results obtained were as follows:

Series.	No. of Plates.	Colour.	Relative Mean Loss in Weight.
I.	1–5	White	100
V.	21–25	Green	27
III.	11–15	Yellow	28
II.	6–10	Red	0
IV.	16–20	Black	42

As we pass from white to the red end of the spectrum the protection afforded by the paint is greatly enhanced. The plates painted with red lake showed hardly any corrosion. The green colour was obtained by mixing the blue and yellow lakes, and the similarity of the results with green and yellow paints was perhaps to be expected.

The black paint afforded less protection than the yellow, green, and red, although theoretically it might have been expected to afford the best protection of all. The explanation probably lies in the fact that the pure black lake mixed with such difficulty with the oil that it could not be conveniently worked up into a paint. It was therefore mixed with an equal weight of the white barium sulphate before incorporation in the oil, and the colour of the resulting paint was thus not a dead black.

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[1] This was really a mixture of 50 per cent. pure black dye and 50 per cent. barytes, for the reasons given below.

The foregoing series of experiments apparently indicate that the most permanent paints are those containing dark or red pigments, other things being equal, inasmuch as these pigments absorb the chemically active rays of light. White paints and those nearer the blue end of the spectrum, on the other hand, more readily disintegrate, as the shorter waves of light are reflected into the oil, thereby catalytically accelerating its destructive oxidation. Dark paints are thus specially to be recommended for the protection of iron and steel exposed to daylight.

These results are interesting in view of the observations of the Inspection Committee on a series of paint tests carried out in North Dakota.[1] These tests were begun in 1906, and consisted of a large number of boards painted with various mixtures and exposed to the air. It was found that "The coloured formulas in every case showed a great superiority over the same paints in white untinted, and demonstrated that a percentage of colour has a wonderful influence on the preservation of the paint coating, reducing chalking, checking, and disintegration."

The explanation offered by the Committee for this protective action is that it is "probably due to the reinforcing value of the colour pigments used." The meaning of this is not quite clear, but presumably refers to the mechanical properties of the pigments.

It would appear, however, that the true explanation is the optical one suggested above.

COARSE AND FINE PIGMENTS.

It is well recognised in practice that a very coarse material does not form a suitable constituent for paint, and that if an efficient paint is required its pigmentary particles must be reduced to very small size. This received striking emphasis in connection with the deterioration of steelwork in the New York Underground Railway several years ago.[2] The metal had been painted with a mixture of 84 per cent. of red lead and 16 per cent. of lin-

[1] Gardner, *Paint Technology and Tests* (New York, 1911).

[2] *Bayerisches Industrie und Gewerbe-Blatt*, 1906, No. 30.

seed oil. After $2\frac{1}{4}$ years the paint film exhibited serious cracking, and removal of the coating laid bare considerable areas of rusted metal. Microscopic examination proved that the source of the trouble lay in the coarseness of the red lead, which hindered close combination of pigment and oil, so that the paint was abnormally porous to moisture.

Now the total superficial area of a given weight of pigmentary particles is inversely proportional to their diameter—assuming them to be spherical in shape. Thus if a sphere of unit size is crushed into particles only one-tenth of the original diameter their total superficial area is increased tenfold; from which it is clear that the finer the pigment the more intimate is its association with the oil, and the more efficient the paint, since the particles may be more closely packed together, thus rendering the coating less porous to air and moisture. Several questions of great practical importance immediately suggest themselves, namely:

1. To what extent should the pigmentary particles be reduced in size?

Evidently they should have a smaller diameter than the thickness of the coat of paint to be applied, otherwise they will project from the surface, rendering it more liable to mechanical injury.

In a well-ground pigment the particles may be expected to vary from 0·002 to 0·026 millimetre. In considering the advisability of reducing the size appreciably below this it is necessary to remember that:

(i) The finer the pigment the greater is the spreading power, and if this is increased beyond a certain limit the "body" or hiding efficiency becomes too weak for practical purposes.

(ii) Beyond a certain working limit the cost of grinding a pigment to a still smaller size is increased out of all proportion to the reduction in size. It may be cheaper, therefore, to paint a steel structure twice with a good medium paint than once with a highly expensive mixture.

2. Does a pigment yield the best results for each grade of coarseness with the same proportion of oil, or has each grade of fineness its own optimum concentration?

3. Is it most efficient to employ pigmentary particles of uniform size?

This point was studied by Perry,[1] who concluded that "the requisite thickness of a paint film, together with the utmost attainable strength and impermeability, can best be obtained by a properly proportioned blend of pigments of three or more determinate sizes." The theory is that, with particles of different sizes, a more compact, dense, and impervious mixture can be obtained than when the sizes are all uniform, since the smaller particles tend to fill in the spaces between the larger ones. Therefore "the least voids occur when the voids between the large particles are filled with smaller particles, and when these smaller voids between the smaller particles are in turn filled with still finer particles. In other words, particles with three determining sizes will fill up a given space more completely than particles of two determining sizes, and very much more completely than particles of one size."

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[1] See Gardner, *Paint Technology and Tests* (New York, 1911).

It was the present author's intention to investigate each of these problems with field tests, but up to the present only the following results have been obtained.

Two grades of Venetian red were chosen, one being of the usual quality, whilst the other had been more finely ground, but both samples came from the same source. Plates painted with these were exposed to the air for seven months. The relative losses in weight due to corrosion are given in the accompanying table:

Series.	No. of Plates.	Composition of Paint by Weight.	Grammes of Paint on each Side.	Mean Loss in Weight.
XIV.	109–113	50 V.r.[1] 50 oil No. 6	9·0	7·94
XX.	139–143	50 fine V.r. 50 oil No. 6	9·0	5·50

The finer pigment worked much more easily than the coarser, and yielded a superior surface. The foregoing figures indicate that it constitutes a more efficient paint.

SHOULD SCALE BE REMOVED BEFORE PAINTING?

As is well known, when iron leaves the mills it is coated with scale or blue-black ferroso-ferric oxide, which adheres very tenaciously to its surface. So long as this covering remains intact it affords a very efficient protection against corrosion; but if for any reason it is rendered discontinuous the exposed portions of the underlying metal rapidly rust and the corrosion continues underneath the adjacent layers of scale, which now begin to peel off. If the metal happens to have been painted, the paint will peel off with the scale. Accordingly, many painters prefer to remove all scale before painting. This may be accomplished by sand-blasting or pickling. At least one large firm allow their steel structures to stand exposed to the weather, after erection, without any covering of paint, and when corrosion has proceeded to a sufficient extent to loosen the scale, the rust and scale are scraped off and the metal is given its first coat of paint. These processes, however, are a source of loss, because not only do they take time, but they involve the wastage of a certain amount of good metal in removing the adherent scale. It seemed important to determine, therefore, if this procedure was really necessary. To this end thirty plates were taken, fifteen with scale on (plates 89 to 103), and fifteen from which the scale had been removed by the sand-blast (plates 104 to 118). These were painted on each side with the same weight (9 grammes) of 50 per cent. Venetian red paint (for details see the table, p. 120), and exposed to the air for periods ranging from five to ten months. For the sake of convenience the results may be summarised as follows:

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[1] Venetian red.

Series.	Plates.	Condition of Plates.	Length of Exposure. (Months.)	Mean Loss due to Corrosion. (Grammes.)
X.	89–93	Scaled.	5	2·31
XIII.	104–108	Sand-blasted.	5	3·81
XI.	94–98	Scaled.	7	3·13
XIV.	109–113	Sand-blasted.	7	7·94
XII.	99–103	Scaled.	10	3·20
XV.	114–118	Sand-blasted.	10	5·90

In every case the appearance of the scaled plates was much superior to that of the sand-blasted ones, and the loss in weight due to corrosion is seen to be very much less. In fact, the superiority in this latter respect of the scaled plates was considerably greater than would appear from the above table, because the loss in weight of the sand-blasted plates is that due entirely to the corrosion of the metal, whereas the loss experienced by the scaled plates is that due to loosened scale, as well as to oxidation of the iron itself.

An attempt was therefore made to determine the approximate weight of scale on the plates. It could be seen to vary very considerably in thickness, both on different plates and on different parts of the same plates. There is no accurate method of determining the amount of scale on such plates. Mechanical cleaning cannot be adopted as with ordinary rust, owing to the tenacity with which the scale clings to the metal. An approximate and very useful method consists in immersing the plates, already weighed, in dilute sulphuric acid, whereby a thin layer of the metal dissolves, loosening the scale. The plate is now washed and re-weighed. The amount of dissolved iron in the acid is estimated by titration with permanganate, and the difference between that amount and the loss in weight of the plate clearly gives the weight of scale. This, of course, assumes that the scale has undergone no chemical change. Probably the scale undergoes slight reduction in contact with the nascent hydrogen, and the estimated amount is somewhat too low;[1] but the error is certainly small, and is very much less than the variation in the amounts of oxide on the different plates. Four plates were dealt with in the above manner, the acid being contained in a large leaden trough. The first two plates were chosen because the amount of scale on them was apparently equal and somewhat thin. The third plate represented a good average, whilst on the fourth the amount of scale was very much above the average. The plates thus include the extremes used in this research.

The amounts of oxide were found to be:

	Grammes.
Plate 1	8·89
,, 2	8·96
,, 3	11·44
,, 4	14·15
Mean	10·86

The average plate, therefore, might be regarded as carrying from 10 to 12 grammes of scale, or from 2·5 to 3 grammes per square foot. It is not improbable, therefore, that in the preceding table in which the scaled plates are stated to have lost from 2 to 3 grammes in weight, at least half of this was due to scale, so that the actual amount of iron corroded was proportionately small, a fact which materially enhances the observed superiority of the scaled plates. One other point remains to be considered. The presence of scale is usually regarded with suspicion, as tending to cause pitting during corrosion. This certainly is the case where the metal is completely immersed in water, since the liquid water is an excellent medium for promoting local activities of this kind. In the case of structures exposed to the air, however, pitting is hardly likely to occur to any serious extent, and certainly not to any greater extent than by allowing the plates to first rust in air without any paint in order to loosen the scale. Evidently, therefore, *the cheapest method, and the one best calculated to prolong the life of the metal, is to paint structures while their scale is still on, after, of course, removing any loosely adherent flakes and rust. The coat of paint will last rather longer than it would if applied to the pickled or sand-blasted surface, and the labour and time involved in removing the scale are saved. When the coat of paint is worn out, it should be scraped off, together with any loosened scale and rust, and the structure re-painted again in the ordinary way.*

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[1] In the case of ordinary rusting this reduction is very considerable, and this method cannot be applied with accuracy. See Friend and Marshall, *Journal of the Iron and Steel Institute*, 1915, No. I. p. 353.

The Painting of Rusty Surfaces.

Closely allied to the foregoing is the question of painting a rusty surface. In practice it is usual for the painter to carefully scrape away any rust prior to applying the paint. Undoubtedly it is essential to scrape away any hard lumps of rust or loose skin of magnetic oxide; theoretically, however, a slight coating of fine, uncaked rust might be an advantage rather than otherwise if a thin paint were applied. And this for two reasons:[1]

1. Rust is practically a pure ochre. Hence by applying a thin paint that contains a high percentage of oil, a similar result is obtained as by first cleaning the metal and then applying a coat of thicker paint.

2. If the rust is removed by scraping or with sandpaper a smooth, metallic surface remains which offers but little bite or grip for the paint. If, however, the rust is allowed to remain, the under-surface of metal is somewhat rough and the paint has an opportunity of adhering more closely.

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[1] Friend, *Carnegie Scholarship Memoirs*, 1912, vol. iv.; 1913, vol. v.

In some preliminary experiments carried out with plates completely immersed in water it was shown[1] that the above argument was correct, corroded plates suffering considerably less additional loss after painting and prolonged exposure than the same kind of plates first polished and then painted and exposed.

It seemed important to determine whether or not this applies also to plates exposed to air. To this end ten plates were exposed on the fence for one month. Five of them were then cleaned with sandpaper, the mean loss in weight of four of them being 1·44 gramme (see p. 88). The fifth plate yielded an irregular result, which was discarded. The ten plates, five rusty and five cleaned, together with five pickled plates, were then painted with 12 grammes of 40 per cent. Venetian red paint on each side, and exposed to the air for two and a half years. The results were as follows:

Series.	No. of Plates.	Condition of Surface.	Mean Loss in Weight. (Grammes.)	Relative Corrosion.
LI.	291–295	Rusty, containing 1·44 gramme of rust.	2·94 − 1·44 = 1·50	100
LII.	296–300	Fairly smooth. Sandpapered.	1·13	75
LIII.	301–305	Pickled. Very smooth.	1·55	103

The results are not very conclusive but appear to show (1) that the presence of rust is not very harmful, and (2) that pickled plates are more readily corrodible than those cleaned by mechanical means.

Summary and Conclusions.

The following summary and conclusions refer to painted ironwork exposed to aerial corrosion.

1. The practical value of acceleration tests is shown to be very small in the present state of our knowledge. Reliable results can only be obtained from tests carried out under conditions closely resembling those required in practice.

2. Addition of pigment to oil increases the efficiency of the latter as a protective paint until a maximum is reached. After this, further addition of pigment causes deterioration. The

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[1] Friend, *loc. cit.*

best results are obtainable from paints possessing as high a percentage of good oil as is compatible with good body and any other working property that has to be considered.

3. Linseed oil on setting expands by some 3·3 per cent. This is the primary cause of crinkling. Further oxidation causes a decrease in volume. This in time leads to cracking.

4. Linoxyn is permeable to moisture. The permeability is reduced by heating in absence of air, the oil increasing in density, viscosity, and molecular weight.

5. Polymerised linseed oil affords a better protection than raw oil when used as a paint vehicle.

6. The functions of a pigment are to toughen the film and render it less permeable to water vapour and oxygen. It also reduces the expansion of the oil on setting and thus minimises the tendency to crinkle.

7. A thick coat of paint protects the underlying metal more efficiently than a thin coat, provided the coat is not so thick that running or crinkling takes place.

8. The very best results are obtained by multiple coats. Two thin coats are better than one thick one of equal weight.

9. Thinners enable thin coats of paint to be applied. Turpentine leaves a very slight residue behind upon evaporation, but its effect on the efficiency of the paint is small.

10. Other things being equal, the most permanent paints are those containing black or red pigments, since these absorb the shorter rays of light and prevent them from hastening the destructive oxidation of the linoxyn by the air.

11. Finer pigments afford more efficient protection than coarse pigments, since they are more thoroughly in contact with the oil.

12. Iron structures should be painted whilst their scale is still on after loosely adherent flakes and rust have been scraped off. The paint will last rather longer than if applied to the pickled or sand-blasted surface, and the labour of removing the scale is saved.

13. Experiments with rusty plates are not conclusive, but suggest that the rust need not be so carefully removed, prior to painting, as is usually thought to be necessary.

Finally, the author wishes to express his indebtedness to the Carnegie Scholarship Committee for a grant which has enabled the present research to be carried out.

TABLE OF RESULTS.

(All weighings are expressed in grammes.)

Series.	Surface of Plate.	Composition of Paint by Weight.	Weight of Paint on each Side.	Exposure to Weather. (Months.)	Plate No.	Loss in Weight.	Mean Loss.	Relative Corrosion.
I.	Sand-blasted	First coat: 120 white lake 30 oil No. 8 Second coat: 90 white lake 30 oil No. 8	First coat: 25 Second coat: 18	27	1 2 3 4 5	1·75 1·30 1·04 1·94 2·13	1·63	100
II.	,,	First coat: 120 red lake 30 oil No. 8 Second coat: 90 red lake 30 oil No. 8	,,	27	6 7 8 9 10	0·30 −0·40 0·25 −0·08 −0·29	−0·04	0
III.	,,	First coat: 120 yellow lake 30 oil No. 8 Second coat: 90 yellow lake 30 oil No. 8	,,	27	11 12 13 14 15	0·38 0·22 0·23 0·80 0·66	0·46	28
IV.	,,	First coat: 120 black lake 30 oil No. 8 Second coat: 90 black lake 30 oil No. 8	,,	27	16 17 18 19 20	0·89 0·64 0·79 0·34 0·78	0·69	42
V.	,,	First coat: 120 green lake 30 oil No. 8 Second coat: 90 green lake 30 oil No. 8	,,	27	21 22 23 24 25	0·47 0·69 0·60 0·40 0·00	0·43	27
VI.	,,	100 Venetian red 200 oil No. 7 50 turps	7	21	26 27 28 29 30	3·55 4·10 4·70 4·00 2·82	3·83	
VII.	,,	,,	10·5	21	31 32 33 34 35	1·80 1·62 1·85 1·95 1·70	1·78	
VIII.	,,	,,	17	21	36 37 38 39 40	1·20 1·70 1·78 1·38 1·00	1·41	

TABLE OF RESULTS—*continued.*

Series.	Surface of Plate.	Composition of Paint by Weight.	Weight of Paint on each Side.	Exposure to Weather. (Months.)	Plate No.	Loss in Weight.	Mean Loss.	Relative Corrosion.
X.	Scaled	50 Venetian red 50 oil No. 6	9·0	5	89	2·40	2·31	
	,,				90	4·65		
					91	0·90		
					92	0·75		
					93	2·83		
XI.	,,	,,	9·0	7	94	3·55	3·13	
					95	4·95		
					96	1·45		
					97	4·50		
					98	1·20		
XII.	,,	,,	9·0	10	99	2·70	3·20	
					100	2·45		
					101	4·05		
					102	3·70		
					103	3·10		
XIII.	Sand-blasted	,,	9·0	5	104	2·85	3·82	
					105	4·15		
					106	3·30		
					107	4·08		
					108	4·70		
XIV.	,,	,,	9·0	7	109	9·08	7·94	
					110	9·05		
					111	6·20		
					112	9·30		
					113	6·05		
XV.	,,	,,	9·0	10	114	6·03	5·90	
					115	5·45		
					116	6·65		
					117	5·80		
					118	5·35		
XVI.	,,	60 Venetian red 40 oil No. 6	9·0	5	119	12·82	15·03	
					120	14·10		
					121	14·20		
					122	17·92		
					123	16·10		
XVII.	,,	,,	9·0	7	124	20·82	20·66	
					125	21·45		
					126	24·62		
					127	15·37		
					128	21·05		
XVIII.	,,	50 Venetian red 50 oil No. 6	14·0	5	129	1·38	1·07	
					130	0·80		
					131	0·80		
					132	1·35		
					133	1·00		
XIX.	,,	,,	14·0	7	134	2·20	2·00	
					135	1·55		
					136	2·25		
					137	2·22		
					138	1·80		

TABLE OF RESULTS—*continued.*

Series.	Surface of Plate.	Composition of Paint by Weight.	Weight of Paint on each Side.	Exposure to Weather. (Months.)	Plate No.	Loss in Weight.	Mean Loss.	Relative Corrosion.
XX.	Sand-blasted	50 fine Venetian red 50 oil No. 6	9·0	7	139	5·40	5·50	
					140	7·20		
					141	3·75		
					142	6·35		
					143	4·80		
XXI.	,,	30 Venetian red 70 oil No. 6	9·0	5	144	0·95	1·12	
					145	1·10		
					146	1·25		
					147	1·10		
					148	1·20		
XXII.	,,	,,	9·0	7	149	0·65	0·93	
					150	1·50		
					151	0·65		
					152	0·95		
					153	0·90		
XXIII.	Pickled	Oil No. 8	4·5	29	154	Oil rapidly destroyed. Metal heavily corroded.		
					155			
					156			
					157			
					158			
XXIV.	,,	50 Deep Indian red 50 oil No. 8	9·0	29	159	2·75	3·04	39
					160	1·50		
					161	2·20		
					162	4·10		
					163	4·65		
XXV.	,,	,,	2 coats: (i) 9·0 (ii) 7·0	29	164	0·80	1·02	
					165	1·20		
					166	0·80		
					167	1·10		
					168	1·20		
XXVI.	,,	50 French ochre 50 oil No. 8	9·0	20	169	2·20	2·24	
					170	2·15		
					171	2·20		
					172	2·15		
					173	2·50		
XXVII.	,,	30 deep Indian red 70 oil No. 8	6·43	29	174	7·15	7·79	100
					175	8·05		
					176	7·95		
					177	9·25		
					178	6·55		
XXVIII.	,,	50 deep Indian red 50 oil No. 8	16	29	179	2·35	1·49	
					180	1·10		
					181	1·20		
					182	1·36		
					183	1·43		
XXIX.	,,	60 deep Indian red 40 oil No. 8	11·25	29	184	1·95	2·37	30
					185	2·60		
					186	2·10		
					187	3·25		
					188	1·95		

TABLE OF RESULTS—*continued.*

Series.	Surface of Plate.	Composition of Paint by Weight.	Weight of Paint on each Side.	Exposure to Weather. (Months.)	Plate No.	Loss in Weight.	Mean Loss.	Relative Corrosion.
XXX.	Pickled	40 deep Indian red 60 oil No. 8	7·5	29	189	3·40	3·05	39
					190	3·05		
					191	3·00		
					192	3·45		
					193	2·35		
XXXI.	„	50 French ochre 50 oil No. 8 20 turps	10·8	20	194	2·10	2·11	
					195	1·45		
					196	3·00		
					197	1·35		
					198	2·65		
XXXII.	„	50 French ochre 70 oil No. 8	10·8	20	199	1·85	1·83	
					200	1·02		
					201	1·60		
					202	3·80		
					203	0·90		
XXXIII.	„	30 red lead 70 oil No. 1	6·43	29	204	6·27	4·52	100
					205	4·05		
					206	4·00		
					207	3·00		
					208	5·28		
XXXIV.	„	40 red lead 60 oil No. 1	7·5	29	209	1·85	2·27	60
					210	1·75		
					211	2·60		
					212	2·65		
					213	2·50		
XXXV.	„	50 red lead 50 oil No. 1	9·0	29	214	1·35	2·16	58
					215	2·00		
					216	5·20		
					217	1·75		
					218	0·50		
XXXVI.	„	60 red lead 40 oil No. 1	11·25	29	219	0·20	0·07	21
					220	0·65		
					221	0·40		
					222	0·40		
					223	0·10		
XXXVII.	„	70 red lead 30 oil No. 1	15·0	29	224	0·60	0·04	19
					225	−0·40		
					226	−0·35		
					227	0·33		
					228	−0·37		
XXXVIII.	„	80 red lead 20 oil No. 1	22·5	29	229	0·60	−1·11	0
					230	−1·80		
					231	−0·43		
					232	−2·77		
					233	−0·80		
XXXIX.	„	80 deep Indian red 20 oil No. 8 43·5 benzoline	33·0 Equivalent to 23·0 without benzoline	29	234	8·9	7·4	
					235	5·9		

TABLE OF RESULTS—*continued.*

Series.	Surface of Plate.	Composition of Paint by Weight.	Weight of Paint on each Side.	Exposure to Weather. (Months.)	Plate No.	Loss in Weight.	Mean Loss.	Relative Corrosion.
XLVII.	Pickled	45 Venetian red 55 oil No. 2	12	31	271	1·10	1·32	100
					272	2·40		
					273	2·20		
					274	−0·65		
					275	1·65		
XLVIII.	,,	45 Venetian red 55 oil No. 3	12	31	276	1·25	2·06	156
					277	3·40		
					278	*		
					279	1·30		
					280	2·30		
XLIX.	,,	45 Venetian red 55 oil No. 4	12	31	281	1·20	0·74	56
					282	−0·55		
					283	*		
					284	1·20		
					285	1·10		
L.	,,	45 Venetian red 55 oil No. 5	12	31	286	0·40	0·41	31
					287	0·20		
					288	0·15		
					289	0·90		
					290	*		
LI.	Rusty, containing 1·44 grammes of rust	40 Venetian red 60 oil No. 9	12	30	291	*	2·94 −1·44 =1·50	100
					292	1·05		
					293	4·50		
					294	5·75		
					295	3·40		
LII.	Rusty plates cleaned with emery	,,	12	30	296	1·50	1·13	75
					297	2·05		
					298	0.75		
					299	1·25		
					300	0·10		
LIII.	Pickled	,,	12	30	301	0·70	1·55	103
					302	2·50		
					303	0·60		
					304	1·45		
					305	2·50		

* Damaged by falling from fence.

THE EFFECTS OF COLD-WORKING ON THE ELASTIC PROPERTIES OF STEEL.[1]

BY J. A. VAN DEN BROEK.

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF MICHIGAN.

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INTRODUCTION.

STEEL has been intensively studied, especially during the last thirty years. It would appear, however, that most of the research on steel has been conducted by chemists and metallurgists, and has thus been confined to the chemical and metallurgical laboratory. From the metallurgical and chemical points of view, therefore, the subject of "The Effects of Cold-Working on Steel" has been profoundly studied during the last fifteen years, especially in England, by such men as Beilby, Rosenhain, Ewing, and Humphrey. The study of the effects of cold-working on the physical properties of steel, however, seems to be limited to J. Bauschinger,[2] James Muir,[3] and to the recent work by the United

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[1] Received February 19, 1918. Presented at the Annual Meeting of the Institute, May 2–3, 1918.

[2] *Mitteilungen aus dem Mechanisch-Technischen Laboratorium der K. Technischen Hochschule in München*, 1886, vol. 13.

[3] "On the Recovery of Iron from Overstrain," *Philosophical Transactions of the Royal Society of London*, 1900, vol. 193.

States Testing Laboratory at the Watertown Arsenal, Massachusetts.[1] It is stated the tests at the Watertown Arsenal are being continued so that additional information may be expected in the near future.

Bauschinger's work of 1886 to-day stands out pre-eminently as the most advanced treatise on the subject. He experimented mostly on mild steel, and studied the effects of strain in tension and compression on the elastic properties of steel in tension and compression. He also studied the effects of ageing, and to a slight extent the effect of tempering on cold-worked steel.

Muir, who also worked on mild steel, confined himself largely to hysteresis, the effects of cold-stretching, and the effects of tempering at low heats, such as the temperature of boiling water, which he studied in detail.

At the Watertown Arsenal, as stated in its publications to date, experiments with 3·25 per cent. nickel steel were carried out, and the effects of cold-stretching on the elastic properties in tension and compression were studied. Some attention was paid to ageing but none to tempering.

Commercially, the term cold-working ordinarily refers to cold-drawing, rolling, or twisting. In this paper the term will be applied to any process which causes permanent change of shape of steel at a temperature below the critical temperature. An attempt has been made to study the subject in its broadest aspect. Steel has been cold-stretched, cold-compressed, and cold-twisted, and each one of these three kinds of cold-working has been studied as to its effects on the elastic properties of steel in tension, compression, and torsion.

In addition, the effects of tempering cold-worked steel at such low temperatures as the temperature of boiling water have been investigated in connection with ageing.

Materials and Apparatus.

The material considered in this paper has been a low carbon, hot-rolled, mild steel. The chemical composition of a few of the bars tested is as follows, different bars being designated by different letters :

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[1] "Test of Metals," 1915.

TABLE I.

Letter.	C.	Mn.	Si.	Ni.	Cr.	S.	P.
d	0·21	0·40	trace	nil	nil	0·040	0·012
p	0·16	0·27	,,	,,	,,	0·063	0·094
K	0·16	0·26	0·018	,,	,,	0·025	0·006
w	0·26	0·34	0·009	,,	,,	...	0·017
Balls	0·95	0·37	0·27	,,	0·65	0·025	0·025

The tests have all been made by the author in the Testing Materials Laboratory of the University of Michigan. The machines used were one 50,000-pound capacity Riehle tension and compression machine, one 200,000-pound capacity Riehle tension and compression machine, and one 232,000 inch-pound capacity Olsen torsion machine.[1]

It should be borne in mind that these testing machines are straining machines and not loading machines. Strain is here defined as deformation per unit of length, stress as load per unit of area. For example, in conducting a tensile test, after placing the specimen in the machine, the machine is run at a uniform speed. The specimen is strained (elongated) proportionally to the speed of the machine. At first, within the elastic limit, the stresses increase at the same rate as the strains, and correspondingly the loads, which are measured by the machine, increase uniformly. After passing the elastic limit, although the specimen continues to be strained at the same rate, the stress increments are no longer proportional to the strain increments, and the loads registered by the machine ceases to increase uniformly.

TESTS.

The tension tests require little explanation. The specimens were tested by the usual method and gripped between wedge grips. For some purposes the threaded grips may be superior to the wedge grips. However, on account of the large variety of specimens tested and the desire to test the same specimens alternately in tension, compression, and torsion, it was necessary to use wedge grips, and it was found that, with a reasonable amount of care, the experimental error could be reduced to a minimum.

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[1] Moore, "Materials of Engineering," p. 159.

The compression tests have all been performed on specimens not less than 9½ inches and not more than 20 inches in length. The ends of each compression specimen were faced so as to make them perfectly flat and parallel. Plate VII. shows a ¾-inch square twisted bar in the 50,000-pounds capacity machine ready to be tested in compression.

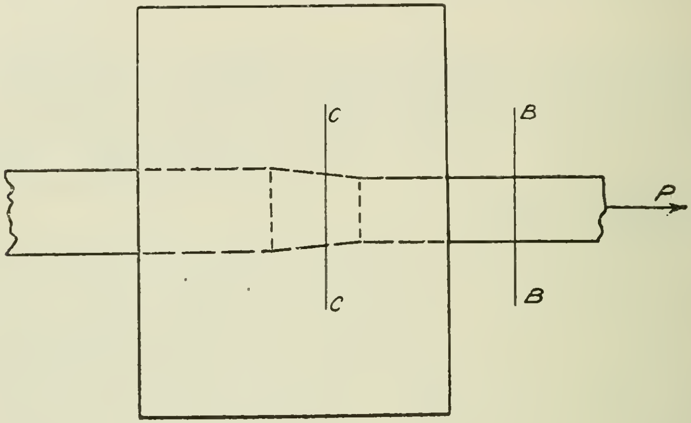

FIG. 1.

Possibly some will question the advisability of using such relatively long compression specimens, *i.e.* for which the ratio l/r is so high. Most experimenters, it seems, have confined themselves, in compression tests, to short columns, sometimes only 1 inch long, presumably to obviate possible errors due to buckling. It appears that one may anticipate two errors in compression tests, one as the result of buckling and another as the result of friction between the bearing blocks and the ends of the specimen. The latter error, it seems, is nearly always present, and its disturbing effect increases as the length of the test specimen decreases. The effect of buckling, although it plays a very important part in structural columns, it is believed may be neglected in laboratory tests, provided the specimen is carefully prepared and the test carefully performed. When buckling does occur, the error is accumulative and marks the end of the test. Similarly, if one is able to load in compression an unbraced specimen 1 inch square and 20 inches long, to a stress of 80,000 pounds per square inch, as illustrated in curves No. 75(f), Diagram II., and curve No. 175(m), Diagram V., and have such specimen support a load of 75,000 pounds indefinitely, one may conclude that the effect of buckling is nil. The horizontal part of curve No. 17(d), Diagram II., illustrated how a compression specimen sometimes may be strained, under a constant load, a considerable distance after the elastic limit is passed, without buckling. Ordinarily, however, buckling sets in as soon as the elastic limit is reached, as is brought out by the fact that most of the curves on Diagram II. and Diagram V. drop rapidly after the elastic limit is passed.

Measurements.

The angular strains in the torsion tests were measured by an arc and pointer clamped 12 inches apart on the specimen.

The linear strains in the tension and compression tests were measured with a Berry strain gauge.

The Berry strain gauge is shown in Plate VII. clamped to a compression specimen ready for a test. It consists of two steel pivots in a steel frame 8 inches apart. One pivot is fixed while the other is part of a bent lever, and rotates freely in a **V** groove. The lever extends inside of the steel frame to a point underneath an Ames dial. The Ames dial registers movement of the end of the lever to $\frac{1}{10,000}$ of an inch. Referring to Plate VII., the top pivot is fixed while the lower pivot is free to move. As the specimen is compressed the two pivots move closer together, and the lever of which the lower pivot is a part moves outward and reacts on the Ames dial at a point inside the steel frame. Previous to placing the strain gauge, two punch marks are made on the specimen 8 inches apart, with a marker the points of which exactly correspond to the points on the pivots of the strain gauge. In order to avoid bending the specimen as the clamp is tightened, a steel plate, slightly sprung, is slipped between the specimen and the clamp. When the strain gauge is clamped on, this bridge, shown in Plate VII., carries the reaction of the clamp to two points exactly opposite the pivots of the strain gauge.

One objection commonly made to the arrangement as described is that the gauge is clamped to but one side of the specimen. This criticism is no doubt qualitatively justifiable. However, experimental error is inevitable with any instrument. It is merely a question as to whether the experimental error seriously impairs the conclusions drawn from the tests. With careful manipulation it appears that this error dwindles into insignificance. In fact, the curves faithfully plotted from laboratory sheets speak for themselves.

THE COLD-WORKING.

The cold-stretching was accomplished in the tension machine by stretching specimens beyond their original elastic limit any desired amount.

The cold-compressing was accomplished in especially designed braces. Plate VIII. shows a 1-inch square specimen in the 200,000-pounds capacity Riehle tension and compression machine, ready to be compressed. One-half of another brace, the one next smaller in size, is depicted to the left in Plate VIII. to show the V groove and the steel lining of the wooden braces, which proved necessary. A set of braces varying by 1 inch in length from 21 inches down to 16 inches were especially designed for the cold-compression process. If, for example, a cold-compressed specimen was desired long enough after cold-compressing to be used in a tension test, a bar of mild steel 1 inch square, 22 inches long, and with both ends faced, was selected. This specimen was first oiled and then clamped in the 21-inch brace, leaving ½ inch of steel projecting outside of the brace at each end. The clamps were very thoroughly tightened to ensure perfect bearing along the entire length of the bar, after which cold-compressing could be commenced. As the compression progressed the specimen naturally increased in size transversely, but this swelling was easily taken up in the wood and in the steel clamps. After compressing a 22-inch specimen to 21 inches in the 21-inch brace, the load was released, the braces taken off, and the operation repeated in the 20-inch brace. In this manner a bar, 22 inches long, could be shortened 3 inches, while maintaining a perfect alignment throughout the cold-working process. The braces were purposely designed long so that the cold-compressed bars might subsequently be tested in tension and have sufficient length to allow space for the grips of the machine and for the strain gauge.

The cold positive twisting was easily accomplished in the 232,000 inch-pound capacity Olsen torsion machine. Difficulty occurred, however, as soon as twisting in a negative direction was attempted. In the first trial the torsion machine was lifted off its base and the specimen twisted out of alignment, because the machine was not designed to perform negative twisting. By providing a suitable steel framework for the recording end of the torsion machine and weighing it down with a few tons of cast iron, 2-inch diameter round bars were sucessfully cold-twisted in two directions.

Tension and compression may be considered as stresses of the same kind but opposite sign. We might intelligibly distinguish between them as one being a positive stress and the other a negative stress. Similarly, right-handed twisting and left-handed twisting may be considered as of the same kind but opposite sign, and for the purposes of this investigation we shall thus distinguish between positive and negative twisting. However, only a positive torque could be measured on the machine.

Discussion of the Data.

The elastic properties of steel considered in this paper are of three kinds—namely, tension, compression, and torsion (shear). Four different kinds of cold-worked steel were each tested for these three kinds of elastic properties—namely, steel as received, steel cold-stretched, steel cold-compressed, and steel cold-twisted.

Two hundred and fifteen specimens were tested, and curves were plotted for each test. Rather than reproduce over two hundred sheets of tabulated data, only curves are here given, and rather than reproduce over two hundred curves, many of which are duplicates, only representative curves have been selected and grouped together for purposes of comparison. Of course, curves differed in different tests. Not always, however, have the most nearly perfect curves been selected for reproduction, but rather curves which were to be compared with one another were obtained, as much as possible, from specimens cut from the same bar, and then plotted on the same plate. No curve is here given without having the properties which it suggests substantiated by several independent tests on different material. If some of the stress-strain curves appear unusually accurate straight lines, they are nevertheless faithful reproductions of laboratory sheets, and it is from the sensitiveness of the curves and the slight deviations from straight lines which one may distinguish, that the author derives his confidence in the significance of the results. As this paper is concerned with the elastic properties of steel, none of the curves are continued to the breaking point. The last point on each curve marks a point well beyond the elastic limit where the strain gauge was removed. Without exception all curves were plotted from the zero point, although the danger of experimental error under low loads, before the test is well under way, is very great. If the specimen is slightly bent, in a tension test, the first increments of load will tend to straighten it, which will cause an erroneous reading of the strain gauge. Possibly the wedge grips do not pull evenly during the first stages of the test, which again may cause an error in strain-gauge reading. In a compression test, the smallest eccentricity in loading, or a minute obstruction between the specimen and the bearing blocks, will cause an erroneous reading of the strain gauge until an adjustment.has been made, after which the strain gauge will record the true elastic behaviour of the specimen. For this reason it is believed best not to attach any special importance to slight positive or negative bends of the curves within low stress values. The essential feature to consider in this discussion would seem to be whether the stress-strain curves beyond stresses of 5000 pounds per square inch are straight lines or not.

A great deal has been written about the definition of elastic limit and yield point of steel.[1] Without presuming to take sides in the different arguments, elastic limit in this paper is understood to be the stress at which the curve first deviates from a straight line. In nearly all cases the point is quite clearly defined on the curves.

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[1] Howard and Linch, *Proceedings of the American Society for Testing Materials,* 1915–1916.

By yield point is meant the stress at which the steel begins to deform very rapidly under very small increments of stress. Although not so clearly defined as the elastic limit, it is nevertheless necessary to refer to it occasionally.

The meaning of the different numbers and letters on different curves is explained as follows. The numbers refer to the order in which the tests were made; the letters in brackets after each number refer to the bar from which the specimen was cut. If the elastic properties of specimens were to be compared with one another, the specimens were, as much as possible, cut from the same bar, and thus, although having a different number, are designated by the same letter in brackets following the number.

The curves are to some extent self-explanatory. The type of test they represent is printed on each curve, as much as possible, in order that the diagrams may be studied independently of the text. All curves on each diagram, although representing specimens cold-worked in different manners, represent one kind of test only—namely, tension, compression, or torsion. The only exception is in Diagram IX., where one compression curve is shown along with two tension curves. The diagrams showing tension and compression curves need little explanation. The stress is the load per unit area; the strain is the deformation (lengthening or shortening) per unit of length. The degree of cold-stretching or cold-compressing is expressed in percentage, which was obtained by computing the difference between the original and the final gauge length of the specimen and dividing that difference by the original gauge length.

The slope of stress-strain curves is a measure of the modulus of elasticity, or of rigidity. All curves with the same slope, therefore, have the same modulus of elasticity or modulus of rigidity. Torsional stress-strain curves are frequently seen plotted with the torque as abscissa and the angle of twist as ordinate. Since the torque varies as the cube of the diameter and the angle of twist varies inversely as the diameter, one naturally obtains in such a case two entirely differently sloping curves for two shafts that are essentially the same and differ only in diameter. The curves in Diagrams III. and VI. are all plotted from data reduced to units corresponding to the units plotted on the tension and compression stress-strain curves—namely, stress at the extreme fibre figured from the formula $f = \frac{16\ T}{\pi\ d^3}$ and strain at the extreme fibre from the formula $\delta = \frac{\phi \times r}{l}$. With these units torsional stress-strain curves will have the same slope when the modulus of rigidity of different specimens is the same, regardless of differences in diameters of the shafts. In an attempt to reduce the degree of cold-twisting to standard units, the degree of cold-twisting of specimens, the stress-strain curves of which are plotted on Diagram VI., is expressed in a percentage as radians of twist per radian of length. Thus a 3-inch shaft twisted one revolution in 12 inches would be said to be cold-twisted, $\frac{2\pi \times 1{\cdot}5}{12} = 0{\cdot}787$ radians per radian $= 78{\cdot}7$ per cent.

On Diagrams III., IV., V., VI., and IX. the origin for each curve was shifted so as to avoid overlapping of curves.

Diagrams I., II., and III. are similar and should be studied in conjunction. Diagram I. shows steel cold-worked in four different ways and subsequently tested in tension. Diagram II. shows a similar set of specimens tested in compression, and Diagram III. shows a third set cold-worked in four different ways but tested in torsion.

Curve No. 25(d), Diagram I., shows a stress-strain curve for a bar of mild steel "as received," tested in tension. By "as received" is meant the state of the steel in which it was received at the laboratory, viz. hot rolled and covered with mill scale. It may be noticed that the major part of curve No. 25(d) is horizontal until it runs off the plate. This of course does not mean that the steel broke at that point or that the steel could be strained indefinitely without producing any increase of stress. In order to plot curve No. 25(d) to the same scale, until its maximum stress was reached, we should require a diagram ninety times the length of Diagram I. After the data for curve No. 25(d) were obtained, the strain gauge was removed and the bar was continued to be strained until a maximum stress of 58,800 pounds per square inch was reached. It was then taken out of the machine, boiled for fifteen minutes, and tested again as No. 27(d). Note that the elastic limit of No. 27(d) comes at about 66,000 pounds per square inch, or 12 per cent. beyond the stress at which the cold-stretching was discontinued.

Also note the high ductility, 64·7 per cent., as expressed in percentage reduction of area, coincident with this high elastic limit. In fact, the effects of cold-working on the elastic properties of steel seem to be independent of the stresses involved in the cold-working process, but seem to be a function of the strains produced in cold-working, regardless of how such strains are brought about. Curve No. 22(d), Diagram I., and curve No. 21(d), Diagram II., were obtained from a piece of steel cut from the same stock as No. 25(d) and No. 27(d), cold-twisted, then cut in two, and one part tested in tension as No. 22(d), Diagram I., and the other part tested in compression as No. 21(d), Diagram II. These two curves are very similar indeed, which suggests that cold-twisting modifies the tensile elastic properties of steel similarly to the way it modifies its compressive elastic properties.

Curve No. 75(f), Diagram II., was obtained from a specimen cold-compressed 15·6 per cent., then boiled, and then tested in compression. It is seen that, just as cold-stretching raises the elastic limit of steel in tension, so cold-compression raises the elastic limit of steel in compression.

Curve No. 80(m), Diagram I., was obtained from a specimen cold-compressed 8·1 per cent., tempered in boiling water and tested in tension. Curve 77(d), Diagram II., was obtained from a specimen cold-stretched 24·1 per cent., boiled and tested in compression. Both curves show an elastic limit of the same value as the original elastic limit but a somewhat raised yield point.

Diagrams IV., V., and VI. were compiled for the purpose of bringing out the significance of time and temperature effects on cold-worked steel.

It is seen from curves No. 171(p), No. 78(d), and No. 172(p), Diagram IV., from curves 176(m) and 175(m), Diagram V., and from curves 182(v) and 183 (v), Diagram VI., that if steel is tested in the direction in which it was cold-worked, very soon after cold-working, the elastic limit is lowered below the original elastic limit, often down to zero, and the yield point comes about at the stress at which cold-working was discontinued. If the specimen is aged for a short time (curve No. 78(d), Diagram IV.), the yield point is raised but the elasticity is not perfected; if the specimen is tempered, however, at a heat of about 100° C. or more, the elasticity of the steel is perfected and the elastic limit is raised from 10 per cent. to 20 per cent. beyond the stress at which cold-working was discontinued. Curves of aged specimens, other than the one here shown (No. 78(d), Diagram IV.), have shown occasionally greater improvement in the elastic properties of steel, as the result of ageing, but never have the effects of ageing a hundred days proved equal to the effects of tempering. It is believed, however, that if sufficient time is allowed, ageing will perfect the elasticity of cold-worked steel to the same extent that tempering at low temperature does.

After the diagrams were made up, a possible source for misinterpretation was noticed in the way curves A, No. 171(P), No. 78(d), and No. 172(P) are shown in relation to one another on Diagram IV. It is to be noted that No. 171(P) and No. 172 (P) are strictly comparable. They were of the same specimen, in one case tested immediately after cold-working; in the second case tested after tempering for a few minutes at 100° C. Curve No. 78(d) was of an entirely different specimen, and is strictly comparable to curve No. 27(d), Diagram I. In its position on Diagram IV. it shows clearly that ageing 114 days did not perfect its elasticity beyond its original elastic limit; that is to say, the curve approaches the original tangent but does not coincide with it. It might, however, also lead one to suppose that ageing did not raise the yield point. This is not the case, as a similar specimen without ageing not only departed further from a straight line, but had its yield point 10 per cent. lower; and a third specimen, cold-stretched exactly the same amount and boiled, was like curve No. 27(d), Diagram I., with its curve perfected but its yield point at about the same value as that reached by ageing 114 days

On the specimens tested in a direction opposite to the direction of cold-working (curves No. 114(t), 115(t), and 112(t), Diagram IV., curves 180(w), 178(w), and 177(w), Diagram V., and curves 146(v) and 147(v), Diagram VI.) the effect of ageing and tempering is seen to be even more pronounced. When a specimen is tested within ten minutes after cold-working, in a direction opposite to that in which it was cold-worked, the elastic limit is seen to be zero (curves 114(t), Diagram IV., 180(w), Diagram V., and 146(v), Diagram VI.). If aged for a few days, the elasticity is partly restored, but in no case comes up to the original elastic limit (curves No. 115(t), Diagram IV., and No. 178(w), Diagram V.). If heated to 100° C. or a little more, the elasticity of the specimen is perfected up to or somewhat above the original elastic limit (curves No. 80(m), Diagram I., No. 77(d), Diagram II., No. K.65, Diagram III., No.112(t), Diagram IV., No. 177(w), Diagram V., and No. 147(v), Diagram VI.).

Curve No. 181(m), Diagram V., shows the elastic properties of steel which was cold compressed 11·6 per cent., then boiled, then cold stretched 7·5 per cent., then boiled and subsequently tested in compression.

The horizontal portion of the stress-strain curves, so pronounced in many of the curves, may be explained as follows. The engineer defines elastic limit as the stress at which the stress-strain curve departs from a straight line. The metallurgist defines it as the stress at which some of the steel grains begin to break up (grain failure along slip bands). The two values exactly coincide. The breaking up of the crystals, however, requires time and energy. In a bar machined down in the middle it usually begins in the centre. In a bar of mild steel gripped in wedge grips, it always begins between the wedges, because the strain conditions at that point are a maximum, being the result of the combination of high compression stresses, due to the wedge grips, and high tensile stresses, due to the machine loading. If the straining (elongating) of the specimen continues uniformly, the rupturing of the crystals progresses from the centre towards the ends, or in case of wedge grip arrangement, from the ends towards the centre, under a uniform stress, until all the crystals throughout the entire length of the bar are ruptured, after which the stresses will increase again, more or less proportionally to the rate of increase of the strains. It should be remembered that the modern testing machine is a straining machine and not a stressing machine.

When a bar of mild steel is strained sufficiently to start some of the crystals rupturing and the machine is then stopped, the specimen will come to equilibrium under a stress such that a little more stress will result in more crystals rupturing; a continuation of that stress or any value less than that stress will leave the specimen in a state with some of its crystal grains ruptured, while others are still intact. This process might be likened somewhat to a line of dominoes set on end. One is caused to fall against an adjoining one, and the whole line will fall as long as conditions are kept constant. When steel is strained and crystals begin to break up, one crystal which fails diverts more stress to its neighbour, this adjoining crystal breaks and in turn causes the next one to break, provided the stresses are kept constant. In the ordinary testing machine, however, the stress cannot easily be kept constant under such conditions. Therefore, when the machine is stopped after the yield point of the specimen is passed, the crystals keep on rupturing for a short time, the specimen correspondingly elongates a little and the load correspondingly drops slightly. The load to which the machine settles down after a specimen of mild steel has been stressed slightly beyond the yield point, but before the crystal grains are disturbed throughout the entire length of the bar, the author has found, corresponds exactly to the elastic limit. If the specimen is being elongated uniformly and continuously, the horizontal part of the curve will run a little higher than if the machine is stopped at intervals and readings taken when the interior of the bar has reached a stage of equilibrium. This is easily explained by the fact that it requires a greater stress to rupture crystals throughout the length of the specimen at a rapid rate than it does at a slow rate.[1]

COLD-STRETCHING STEEL DOES NOT LOWER ITS ELASTIC LIMIT IN COMPRESSION.

In nearly all the literature of the last twenty years on the effect of overstrain on steel, the statement occurs that cold-stretching, although raising the elastic limit in tension, lowers the elastic limit in compression.

Rosenhain, one of the most enthusiastic exponents of Beilby's amorphous cement theory, writes in his Introduction to "Physical Metallurgy," Van Nostrand Company, 1914, p. 247:

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[1] For beautiful photographs illustrating this point, see *Commission des Methodes d'Essai des Matériaux de Construction, Rapports Particuliers,* tome ii., 1900.

"There is one difficulty about the explanation of the hardening of metal by plastic strain, as given by the conceptions explained above, which requires brief mention. This lies in the fact that the hardening produced by plastic strain is, in certain cases at all events, unidirectional. For instance, a piece of steel which has been 'hardened,' *i.e.* has attained a raised yield point and apparently raised elastic limit, as the result of tensile overstrain, is not really hardened in every way, for, if it is tested in compression, it is found that for stresses of that kind the apparent elastic limit has been lowered, so that the total range of stress of elasticity, from the limit in compression to the limit in tension, has not been materially altered. It is difficult to see how the formation of hard amorphous layers on surfaces of slip can account for softening of the metal in relation to compression while producing hardening as against tension. It may be, of course, that there is something directional about the manner in which the crystalline arrangement is broken up on the slip surfaces, so that a configuration results which allows of slip in one direction but not in another."

And James Muir writes in his article on "The Recovery from Overstrain," *Phil. Trans.*, vol. 193, p. 45:

"Curve No. 4, further, very clearly shows that tensile overstrain—which raises the yield point in tension—lowers that in compression, or, it may be more definite to say, lowers the load at which any arbitrary contraction occurs. This is in agreement with Professor Bauschinger's conclusion with regard to the elastic limits, viz. that the elastic limit in tension cannot be raised without lowering the limit in compression and *vice versâ*. Professor Bauschinger draws a further conclusion from his experiments, namely, that when the elastic limits of a material are varied by overstrain, the range of perfect elasticity seems to remain constant, so that, if the elastic limit in tension be raised, then that in compression is lowered by an equal amount. The author's experiments do not bear this out."

Muir attributes here to Bauschinger the claim that, as the result of tensile overstrain, the elastic limit of steel in compression is lowered an amount equal to the amount its elastic limit in tension is raised, maintaining constant what is called the elastic range. Although other writers on this subject for the last twenty years almost invariably make this statement, it is usually not accompanied by references to its source, and possibly they are mostly quoting Muir's interpretation of Bauschinger's results.

The author, upon studying Bauschinger's data, was unable to find any such statements. On p. 19, statement 2, of *Mitt. aus dem Mech. Tech. Laboratorium der K. Technischen Hochschule in München* of 1886, Bauschinger states the results of his experiments on the effect of stretching on the elastic properties of steel in tension as follows:

"The elastic limit (in tension) is lowered as the result of stretching, often down to zero, so that the specimen, when it is tested immediately after cold-stretching, has no, or else a very much reduced, elastic limit. During the period of rest which follows the cold-stretching, however, the elastic limit increases again. After several days it attains the stress with which it was cold-stretched, and after a sufficiently long period, certainly after many years, it increases to a value even higher than this stress."

On p. 33 of the same article he says with reference to the elastic properties in a direction opposite to the direction of cold-working:

"As the result of stressing in tension or compression beyond the elastic limit, the elastic limit in compression or tension, respectively, is considerably lowered, so much the more, if the cold-working stresses exceed the respective elastic limits by larger amounts and even comparatively small increments of stress beyond the elastic limits, reduce the elastic limit in opposite direction to zero.

"When an elastic limit, thus lowered in one direction, is raised again by stressing in that same direction, and then exceeded, then, at once, the elastic limit in the opposite direction is again reduced to zero, or nearly to zero.

"Time in these processes is without any effect, or at least has very slight influence. That is to say, the elastic limit in tension or compression, lowered by compression or tension, respectively, is not again raised, at least in the course of three or four days, and in the course of the next few weeks certainly only a little, if at all."

It is interesting that this law of Bauschinger's, laid down in 1886, is essentially confirmed by all subsequent research, and also by the work presented in this paper. The generally quoted statement that stretching steel lowers its elastic limit in compression proportionally to the amount it was stretched beyond its original elastic limit, is therefore not substantiated, neither by Bauschinger, nor by Muir, nor by the author, and the author has failed to discover any original data anywhere which seems to substantiate that contention. The apparent discrepancy between the results of different authors seems to be due to the fact that the significance of ageing and tempering has not always been sufficiently emphasised. Bauschinger states that ageing perfects the elastic properties in the direction of cold-working very soon. Scrutinising Bauschinger's and Muir's original data, it does not appear that with ageing they have ever reached a perfect elasticity in the direction in which the specimen was cold-worked, although the deviation from a straight line stress-strain curve was so little that they possibly disregarded it. As regards specimens which were cold stretched and subsequently tested in compression, the same law of ageing seems to hold, only the variations are much more marked. In either case, tension or compression, ageing or tempering, has the tendency to perfect the elastic properties of cold-stretched steel; however, while as regards tension, the stress-strain curve may in a few weeks become so nearly a straight line that it requires a very sensitive test to detect any lack of elasticity, as regards the compressive elastic properties, the amount of improvement necessary to reach perfect elasticity is so large that any shortcoming in it is inevitably detected.

In these experiments, everything seemed to point to the fact that tempering at low temperatures was equivalent to accelerating the effects of time.

Because time was lacking to allow specimens to age properly, curves on Diagram IX. were obtained from a commercially cold-drawn specimen.

By studying the records of the engineering shops of the University of Michigan, the author obtained a piece of $\frac{7}{8}$-inch round steel, commercially called cold-rolled shafting, which was received at least six months ago. It appears safe to consider this stock as cold-drawn, although the trade name may be cold-rolled. It is believed cold-rolling is rarely used except for stock over 3 inches diameter, and certainly not for stock as small as $\frac{7}{8}$-inch diameter.

One specimen cut from this bar was heated to a red heat and allowed to cool in the air in order to obtain a state of metal corresponding to a hot-rolled bar. Curve No. 207(y) gives the stress-strain curve for this specimen. Curve No. 197(y) gives the stress-strain curve of the cold-drawn and aged steel as it was when the author obtained it, tested in tension, and curve No. 201(y) gives the stress-strain curve of a similar specimen tested in compression. It may be noticed how the elastic limit in compression, if anything, is a little above the original elastic limit.

Muir, in a paragraph quoted above, p. 15, incidentally gives results at variance with the results given here. It would seem, however, that his tests on elastic properties are inconclusive because, on the one hand, they were limited in number, and on the other hand the specimens were only $1\frac{1}{4}$ inch long—that is, too small for accurate work.

If the contentions set forth in this paper are correct, it would appear that the strongest evidence Rosenhain mentions against the validity of his favourite amorphous cement theory (p. 139 of this paper) is invalid, and Beilby's amorphous cement theory emerges better substantiated than ever.[1]

THE EFFECTS ON ELASTICITY OF COLD-TWISTING ARE PROPORTIONAL TO THE DISTANCE FROM THE AXIS.

On Diagram I. curve No. 22(d) has the appearance of being approximately a mean between curves No. 25(d) and No. 27(d), and on Diagram II. curve No. 21(d) appears to be an average between curves No. 17(d) and No. 75(f). The natural explanation seems to be that in cold-twisting the outside of the bar is strained severely, and the effect of it on the elastic properties corresponds to curve No. 27(d), while at the centre of the bar the material is strained very slightly, and therefore its elastic properties remain approximately as shown by No. 25(d). When a twisted bar is tested in tension, since its elastic properties vary from the centre to the outside, as from curve No. 25(d) to curve No. 27(d), the resulting curve will be a compromise between the two. If the amount of steel similarly strained was also directly proportional to the distance from the axis, a straight line curve could be expected for the tensile stress-strain curve of a cold-twisted bar. Since, however, the cross-sectional area of steel similarly strained varies as the square of the distance from the axis of the shaft, the curve to be expected is a second degree curve, which is borne out by the experiment. The curves in Diagram VII. were obtained to throw some light on this hypothesis. A $1\frac{3}{4}$-inch round bar was cold-twisted 31·5 per cent. A specimen No. 72(j) was cut from the centre, and another specimen No. 73(j) was cut from the outside, of dimensions as shown on Diagram VII. The elastic limit of both specimens occurs at the same value as that of the original bar. Note that curve No. 73(j) runs not only higher than curve No. 72(j), but that the breaking stress of specimen No. 73(j) is 86,200 pounds per square inch, while the breaking stress of curve No. 72(j) is 69,800 pounds per square inch.

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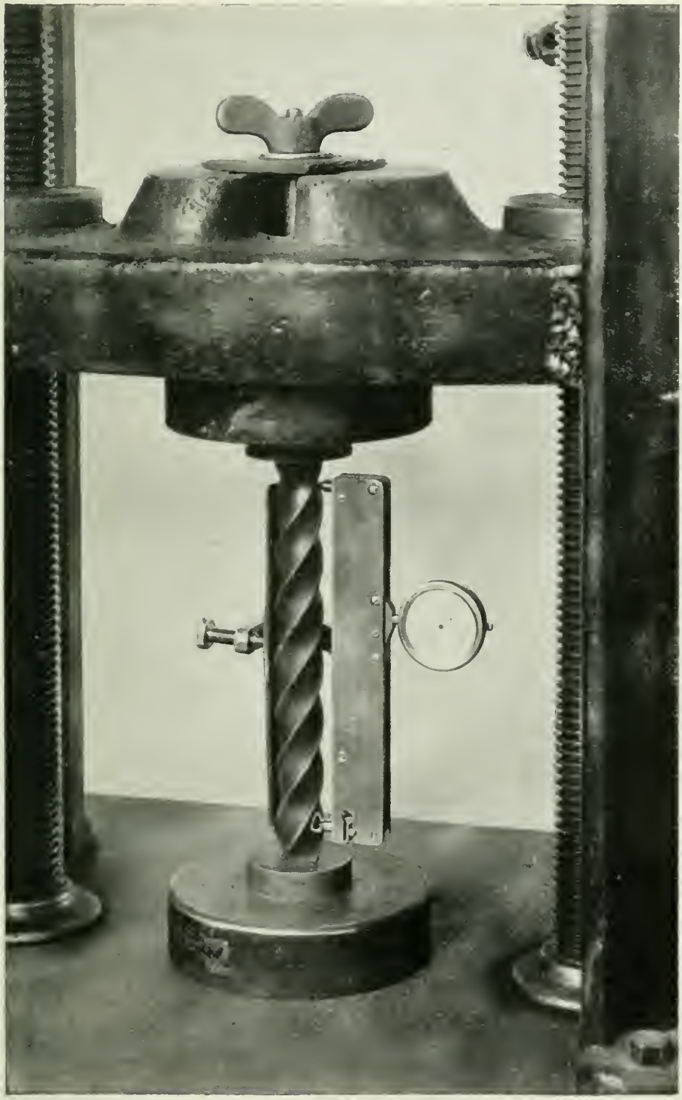
[1] For a more detailed discussion of Beilby's amorphous cement theory, see pp. 148–151 of this paper.

THE EFFECTS OF COLD-WORKING ON THE ELASTIC PROPERTIES OF STEEL ARE PROBABLY A FUNCTION OF THE STRAINS AND INDEPENDENT OF THE STRESSES INVOLVED IN THE COLD-WORKING PROCESS.

The interesting point as to whether the effects of cold-working, here discussed, are dependent on the stresses involved in the cold-working of the steel or are determined by the degree of deformation given to the specimen as the result of cold-working, cannot be fully determined from the results of this investigation. It seems certain, however, that the stresses set up in cold-working have little to do with the changes in elastic properties, and it seems likely that changes in elastic properties of steel are determined by the degree and kind of deformation given to the specimen in the process of cold-working, regardless of what stresses were involved in bringing these deformations about.

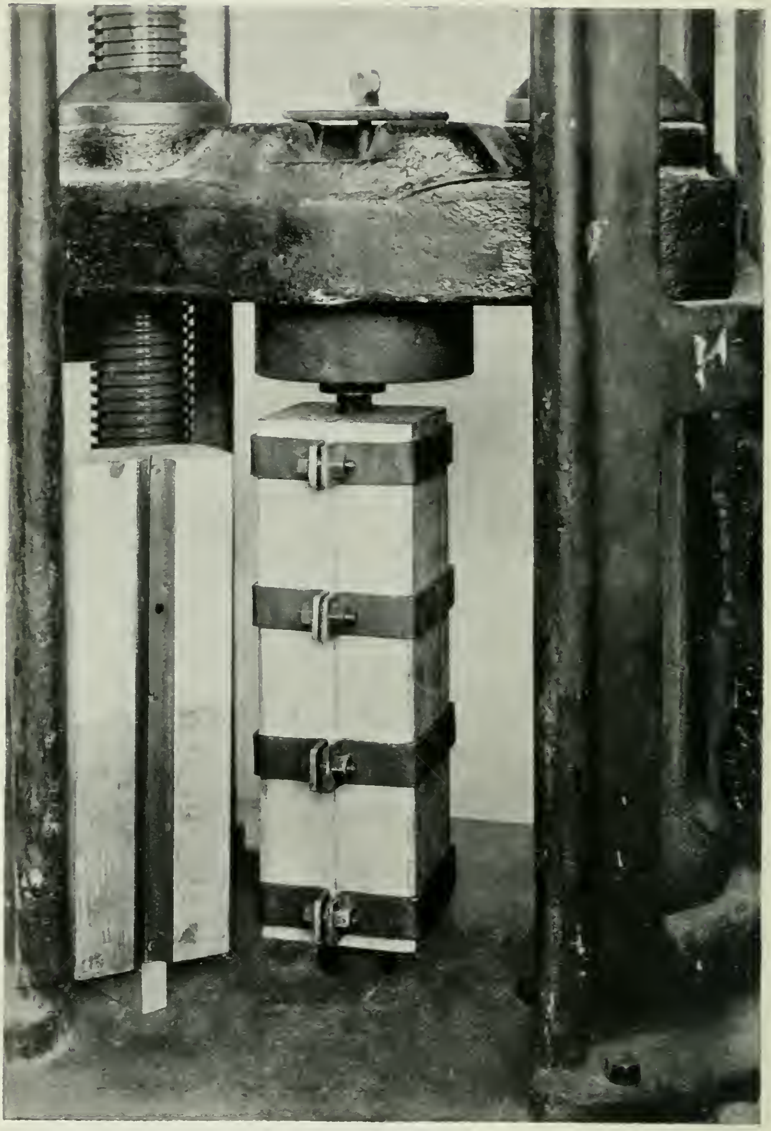
Diagram VIII. is intended to show the effects of cold-working on the elastic properties of steel in a direction at right angles to the direction of cold-working. Curve No. 104(s) shows the stress-strain curve of the steel as received. Curve No. 98(s) shows the stress-strain curve of a specimen cut from the same bar and hammered cold, transversely, in a steam trip hammer, subsequently machined, and then tested in the direction of the longitudinal axis of the specimen. The stresses in the direction of the longitudinal axis of specimen No. 98(s), at no time during the cold hammering process, can have been tensile stresses. The elongative strains, however, in the direction of the longitudinal axis amount to approximately 11·5 per cent. It is seen that cold hammering at right angles to the axis produces effects on the elastic properties of steel in a direction parallel to the axis similar to those obtained by straining under pure tensile stresses. That the curve is not a perfectly straight line was to be expected, since the cold hammering effect, of necessity, differed in intensity throughout the specimen. With strains produced, therefore, which correspond to tensile strains, but unaccompanied by tensile stresses, the change of elastic properties corresponds to those produced by cold-stretching.

To determine whether the cold-working strains or cold-working stresses determine the ultimate elastic properties of cold-worked steel another test was made as follows. It is very noticeable that when a specimen of mild steel is stressed beyond the elastic limit, any amount up to the maximum stress, the beam drops as soon as the machine is stopped, indicating a continued rupturing of crystal grains under constant or slightly decreasing stresses. For example, when specimen (A) of original elastic limit of 32,000 pounds per square inch was stressed instantaneously to 58,500 pounds per square inch, it was found to have been strained 9·4 per cent. The machine was stopped and the beam immediately dropped, indicating that the specimen continued straining under a decreasing load. If it is desired to maintain a constant stress of 58,500 pounds per square inch on the specimen, it is found that the machine must be slowly turned by hand for several hours to keep the beam balanced with a constant load reading. This indicates that straining of the specimen continues for several hours if the steel is once stressed past the elastic limit and kept under a constant load.

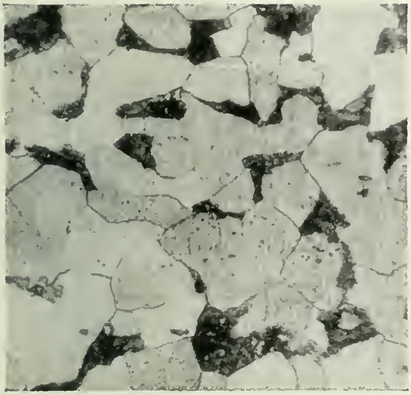


Compression Test Machine with Berry Strain Gauge.

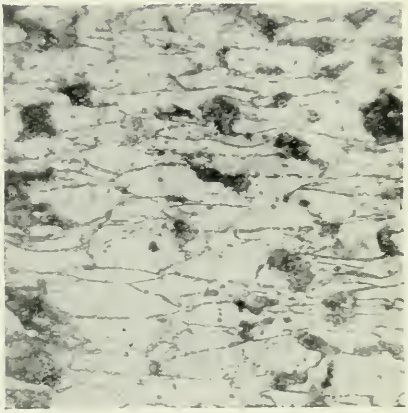
[*To face p.* 144.



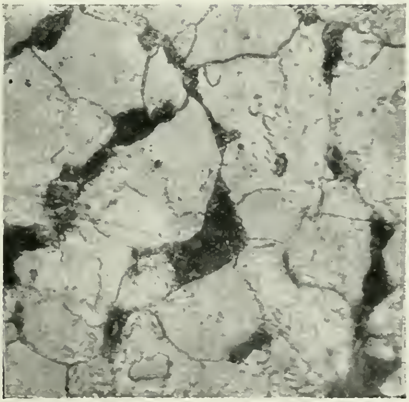
Riehle Tension and Compression Machine.



No. 1.—Longitudinal section of mild steel specimen used in specific gravity test, "as received" (p. 150).



No. 2.—Same steel cold compressed to half its original length.



No. 3.—Transverse section of same specimen, cold compressed.

All magnified 600 diameters, and reduced by one-third.

Three specimens, A, B, and C, of the same bar were prepared. The original elastic limit of the steel was 32,000 pounds per square inch. Specimen A was stressed instantaneously to a stress of 58,500 pounds per square inch, and found to have been strained 9·4 per cent. Specimen B was stressed to a stress of 58,500 pounds per square inch, this stress kept constant for fifty minutes, when it was found to have been strained 12 per cent. Specimen C was stressed instantaneously to a stress of 61,000 pounds per square inch and found to have been strained 12 per cent. Specimens A and B were thus stressed the same amount, but strained differently. Specimens B and C were strained the same amount but stressed differently. The three specimens were boiled together and then tested in tension. Specimen A was found to have an elastic limit of 64,000 pounds per square inch, specimen B had an elastic limit of 67,000 pounds per square inch, while specimen C had an elastic limit of 67,000 pounds per square inch. Since specimens B and C, which were strained the same amount but stressed differently, had the same ultimate elastic limit, and specimens A and B, which were stressed the same amount and strained differently, had different elastic limits, it appears that the effect of cold-working on the elastic properties of the steel is a function of the strain and not of the stress.

Curves on Diagram VII. also indicate a raising of tensile or compressive elastic properties as the result of cold-twisting, without the presence of either tensile or compressive stresses in the direction of the axis of the specimen during the cold-working process.

FATIGUE.

Although no fatigue tests were made in this investigation, it may still be proper to call attention to the relation of the curves on Diagrams IV., V., and VI. to the problem of fatigue. A great many tests have been made on steel subjected to repeated stresses in one direction, and also with repeated stresses in opposite direction. Although all experiments agree in that steel fails under lower stresses when the stresses are repeated or reversed a great many times, some differ as to whether steel can be made to fail, even under reversed stresses, at stresses below the original elastic limit. Possibly the difficulty in measuring the stresses or the neglect to consider the rate at which stress travels, may account for some differences of opinion. It is believed the curves on Diagrams IV., V., and VI. are the first to show accurately how the elastic properties of steel are affected under reversal of stresses within a comparatively short time after the steel has been stressed beyond the elastic limit.

Electric Resistivity of Cold-Worked Steel.

Four specimens cut from a hot-rolled mild steel bar, the chemical composition of which is given under (w) in Table I., p. 127, were cold-worked and subsequently tested for their electric resistivity by Professor Edward D. Campbell of the University of Michigan. The first specimen was tested "as received"; the second specimen was cold-strained 15 per cent. and incidentally stressed to a stress of 57,000 pounds per square inch; the third specimen was cold-compressed 10 per cent., and the fourth specimen was cold-twisted 40° in 1 inch. The electric resistivity for all four specimens was 13·87 microhms at 25° C., indicating that cold-working does not affect in any way the electric resistivity of steel.[1]

The Effects of Cold-Working on the Elastic Properties of Alloy Steels.

Bauschinger, Muir, and the author confined themselves very largely to studying the effects of overstrain on what might be designated as "mild steel." However, twenty-five different bars, many of them obtained from entirely different sources, were used for the tests discussed in this paper. Within the changes in chemical composition, in these twenty-five different sources of test specimens, no variance with the laws of the effects of cold-working on the elastic properties of steel could be detected.

The only extensive work along this line on alloy steel seems to be the work that is being carried on by the U.S. Arsenal at Watertown, Mass.[2]

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[1] For a more detailed discussion of this test by Professor Edward D. Campbell, see Faraday Society of 1918; also articles on "Specific Resistance," *Journal of the Iron and Steel Institute*, 1915 and 1916.

[2] "Test of Metals," 1915.

These tests were confined to a 3·25 per cent. nickel steel, and the results published to date seem to confirm the results presented in this paper. The yield point of a steel with an original elastic limit of 60,000 pounds per square inch is raised to 120,000 pounds per square inch. Since the Watertown Arsenal, to date, did not experiment with torsional tests or with cold compressed specimens, or with the effects of tempering in connection with ageing, no further comparisons can be made. It is shown, however, that to the maximum extent they have aged—namely, seven days, their resultant tests show an imperfect elasticity beyond the original value of the elastic limit of the specimen, just as was the case with specimens tested by the author.

Law Defining the Effects of Cold-Working on the Elastic Properties of Mild Steel.

Diagrams I., II., and III., and also Diagrams IV., V., and VI., reveal striking similarities which suggest that definite laws might govern the effects of cold-working upon the elastic properties of steel. If we distinguish the several kinds of elasticity and cold-working as being of different direction and sense, for example, tension and compression as of the same direction but opposite sense; positive torsion (+ shear) and negative torsion (—shear) as of one direction but opposite sense; but torsion (shear) and tension, respectively, as being of different direction, then we may say:

1. When mild steel is cold-worked and properly aged or tempered and subsequently tested in the same sense as that of the cold-working, its elastic limit may be raised more than 100 per cent. and from 10 to 20 per cent. beyond the stress at which cold-working was discontinued.
2. When mild steel is cold-worked in one direction and properly aged or tempered, but tested in either one of two senses of a different direction, then its elastic limit may be raised some 50 per cent.
3. When mild steel is cold-worked in one sense and properly aged or tempered but tested in the opposite sense, then the elastic limit remains at the value of the original elastic limit, but the yield point is raised.

4. When mild steel is cold-worked in any direction or sense and tested in any direction or sense, without any ageing or tempering, then the elastic limit falls below the value of the original elastic limit, often down to zero.
5. Tempering cold-worked steel at temperatures from 100° to 300° C., or ageing cold-worked steel, has a tendency to perfect its elastic properties. Tempering merely accelerates the effects of time.

The first part of this statement is exemplified by curves No. 25(d) and No. 27(d). Diagram I., curves No.17(d) and No. 75(f), Diagram II., and curves K59 and K64, Diagram III., and by similar curves on Diagrams IV., V., and VI. The second part of the above statement is exemplified by curve K63, Diagram III., curve No. 143(v), Diagram VI., and curve No. 73(j), Diagram VII. The third part of the above statement is exemplified by curve No. 80(m), Diagram I., curve No. 77(d), Diagram II., and curve No. K65, Diagram III., No. 112(t), Diagram IV., No. 177(w), Diagram V., and No. 147(v), Diagram VI. The fourth part of the above statement is exemplified by curves No. 114(t), Diagram IV., No. 180(w), Diagram V., and No. 146(v), Diagram VI.

THEORY EXPLAINING THE EFFECT OF COLD-WORKING ON THE ELASTIC PROPERTIES OF STEEL.

It is hardly the purpose, in this paper, to review exhaustively the contributions to chemical and metallurgical science, of the last twenty years, bearing on the problem of cold-working steel. Certainly, however, to some, the striking improvements in steel as the result of cold-working appear mysterious. One is likely to presuppose that straining steel beyond the elastic limit injures steel permanently. It may not be amiss, then, to review briefly one of the theories advanced to explain the phenomena associated with cold-working of steel.

The amorphous cement theory was advanced by Beilby about 1903 and developed since, particularly by himself, Rosenhain, and Ewing. The following discussion and interpretation of it is made in the light of the facts established in this research.

Beilby and Rosenhain suppose that steel exists in two phases

—the amorphous phase and the crystalline phase. As steel crystallises, the size of the crystals are inversely proportional to the rate of cooling. Different crystals are differently oriented, and when they come together, some steel, encased between them, is unable to align itself with either one of the adjoining crystals. This steel remains in the amorphous state and cements the different crystals into one solid mass. This amorphous cement is supposed to be stronger than the crystalline steel. With a rapid rate of cooling the crystals are smaller, the amorphous cement, which coats all the crystal grains, is naturally greater in quantity and, as is well known, the elastic limit of rapidly cooled mild steel is higher than that of annealed mild steel. It has been shown that when steel is fractured the fracture takes place across a crystal and never along one of the crystal boundaries, which also supports the belief in the superior strength of the cementing material over the crystalline material. When a steel specimen is stressed increasingly, a stress value is reached at which the large crystals break up into smaller ones. This breaking up of the crystals marks the elastic limit of the steel. This breaking up of large crystal grains into smaller ones occurs along definite cleavage planes (slip bands). Naturally, the crystals oriented most favourably for breaking up along its cleavage planes are ruptured first, while the ones that are oriented less favourably to the direction of the particular stress applied are ruptured later when the stress has become higher. The internal work expended on the metal while being strained transforms some of the crystalline metal into amorphous metal. This amorphous metal hardens but is at first quite plastic. Therefore, when a specimen is stressed soon after cold-working, there is a constant yielding of the amorphous metal under a permanent stress, which makes the specimen as a whole yield more or less. When a specimen is stressed soon after cold-working in a direction opposite to the direction of cold-working, while the newly formed amorphous cement is still plastic, naturally the fractured crystals are tempted to slide back along the slip bands, as much as possible, to their original positions, and the specimen yields in a very pronounced way. This amorphous cement, however, hardens with time, and especially with the gentle application of heat. After a cold-worked specimen is aged, therefore, or boiled in water for fifteen minutes, no plasticity of the specimen is observed. When tested after tempering in the same sense and direction as that of cold-working, most of the planes of weakness have yielded under the cold-working process and renewed breaking up of crystals does not commence, or in other words, the elastic limit is not reached until a stress has been reached higher than the stress at which cold-working of the specimen was discontinued. When a specimen is tested in the same sense but opposite direction from the direction in which it was cold-worked, but after the amorphous cement formed in cold-working has thoroughly hardened by tempering or ageing, breaking up of the crystals does not commence; or in other words, the elastic limit is not reached until after a stress equal to the original elastic limit has been exceeded.

Beilby, Rosenhain, and Ewing advance a great deal of chemical and metallurgical data in support of this theory that steel exists in two phases—amorphous and crystalline. One of the facts advanced is that amorphous steel has a lower specific gravity than crystalline steel, and that therefore cold-worked steel, because of its higher percentage of amorphous steel, has a lower specific gravity than "as received" steel.

Microstructure of Cold-Worked Steel.

Regardless of the conclusions drawn from it, the fact that cold-working steel lowers its specific gravity has been well substantiated by independent investigators.[1] The author, also, has cold-compressed three specimens of mild steel 1 inch × 2 inches, and three specimens of tool steel $\frac{3}{4}$ inch × $1\frac{1}{2}$ inch to one-half their length, and found a reduction of specific gravity in each case, the average for the six specimens amounting to 0·225 per cent. Photo. No. 1, Plate IX., gives a photomicrograph of the longitudinal section of one of the specimens of mild steel used in the specific gravity test "as received." Photo. No. 2 gives a photomicrograph of a *longitudinal* section of the same specimen "cold-compressed" to half its original length. Photo. No. 3 gives a photomicrograph of a *transverse* section of the same specimen cold-compressed, and taken as near as possible to the point in the specimen where No. 2 was taken. The magnification of all three micrographs was 600 diameters.

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[1] F. C. Lea and W. Norman Thomas, "Change of Density of Mild Steel strained by Compression beyond the Yield Point," *Engineering*, July 2, 1915.

It may be noticed on No. 2 how the individual grains have flattened as the result of compression, and correspondingly it may be seen on No. 5 of the transverse section, taken at the same point, how these same grains have spread. The actual breaking up of these crystals into smaller parts cannot be determined from these photographs. The rupturing of steel grains under stress along slip bands can be observed under the microscope when the specimen is prepared and polished in advance of the test and the specimen strained subsequently,[1] and under favourable circumstances it may be observed with the naked eye.[2] The fractures indicated by the slip bands are covered over if the specimen is polished after being strained, and they are too minute to be detected by the microscope upon subsequent etching of a polished specimen.

Tests on Steel Balls.

Another argument for the existence of amorphous steel was advanced by Beilby and Bengough, in explaining the phenomena of polishing steel by the formation of an amorphous cement on the surface of a steel specimen while being polished. Polishing steel consists of successive stages of grinding and scratching with an abrasive that is harder than steel. The ultimate result is a mirror face that even under a strong microscope does not reveal any scratches. Sometimes, after slight etching with a dilute acid, when some of the outside steel has been removed, scratches may be observed again, indicating that they were merely covered over with something. This something, according to Beilby, Bengough, and others, is amorphous steel worked up on the surface of the steel by the cold-grinding.

When first produced this amorphous steel is like a viscous liquid. It has a considerable surface tension which causes it to smooth out and even cover minute scratches or cracks. It acts similarly to a band of fresh paint. Just after removal of the brush the marks of the hairs are visible, but in a few seconds the surface tension in the fresh paint has caused the ridges to disappear and the paint to present a flat surface. This would thus explain the apparently anomalous fact that successive grinding operations on steel produce a surface which, even under a strong microscope, is free from any abrasive marks.

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[1] Ewing and Rosenhain, *Philosophical Transactions of the Royal Society*, 353A, 1900.

[2] *Commission des Méthodes d'Essai des Matériaux de Construction, Rapports Particuliers*, tome ii., 1900.

The polishing is thus a cold-working operation, the effect of which does not extend beyond the surface.

Because this amorphous steel produced on the surface by cold grinding and polishing is stronger and harder than the crystalline steel in the body of the specimen, it occurred to the author that cold ground and highly polished steel balls may exhibit differences in crushing strength when tested before and after polishing, or after amorphous cement is artificially removed by acid. The author is at present engaged upon a series of tests on steel balls, generously furnished by the Hoover Steel Ball Company of Ann Arbor, Michigan, the results of which it is hoped will be ready for publication soon. Although too early to discuss these tests here in detail, for the purpose of this paper, the following can be stated :

In the manufacture of steel balls the balls are forged, heat treated, rough ground, emery ground, and polished. As the result of two hundred crushing tests on 1-inch balls it was found that the rough ground balls, although slightly larger in size, were 25 per cent. weaker than the polished balls.

Upon etching polished balls for twenty minutes in boiling hydrochloric acid, 25 per cent. solution, their crushing strength decreased 32 per cent. Upon etching rough ground balls and polished balls in similar acid solutions, the same length of time, the crushing strength of the two came down to the same value, indicating that the reduction of crushing strength is not due to the effects of the acid, but rather due to the removal of the amorphous cement from the surface.

Although the amorphous cement theory might lead one to expect a quantitative difference in crushing strength between polished balls and balls which had their polish removed or else tested before they were polished, the author was sceptical before his tests, and expected the difference to be hardly noticeable. The difference of 30 per cent., indeed, seems phenomenal. It may yet be due to other causes which have not been detected. However, it should be borne in mind that although the amount of amorphous cement produced upon the surface of the steel balls by polishing is very little indeed, it is most advantageously placed to increase the crushing strength of steel balls.

The tests on steel balls were made in an especially designed machine, three balls being tested in line.

COMMERCIAL ASPECTS OF COLD-WORKING MILD STEEL.

One of the most desirable properties in steel is a high elastic limit coupled with a fair degree of ductility. Such high elastic limit is usually obtained by alloying steel or by heat treatment, or by a combination of both. However, any process tending to increase the elastic limit nearly always tends to decrease the ductility. In case of nickel steel, which gives a combination of high ductility and high elastic limit, the process of manufacture is expensive.

Possibly the most conspicuous feature of cold-worked mild steel is its high elastic limit coupled with its relatively high degree of ductility. Perhaps a few remarks should here be made about the best measure of ductility. Three different tests for ductility are ordinarily used—the bend test, the test to determine the percentage of elongation, and the test to determine the percentage reduction of area of the fractured specimens. The bend test is not satisfactory, because two specimens may be bent through an angle of 180° and close completely upon themselves and yet be ductile in very different degrees. Furthermore, a bend test is of no use except for very brittle steels, as a $\frac{3}{4}$-inch round steel specimen 0·55 per cent. carbon, which behaves as a hard steel, may be bent to close upon itself, without developing cracks. The percentage of elongation test gives valuable information regarding ductility, but furnishes a poor standard, because on the one hand the results vary for different gauge lengths, and on the other hand the results are affected by the location of the point of fracture, viz. whether the fracture occurs on one of the gauge points, between gauge points or outside of the gauge points.

The percentage reduction of area after fracture can be measured regardless of size of specimen, and gives appreciable values when the percentage of elongation is often too small to be noticed.

The test for percentage of elongation naturally gives relatively small values for cold-stretched specimens, as most of the potential yielding is used up in the cold-stretching processes. Expressed in terms of percentage of reduction of area, cold-worked steel of an elastic limit of 70,000 pounds per square inch may have a reduction of area as high as 65 per cent. As regards the bend test, cold-worked steel of an elastic limit of 70,000 pounds per square inch may be bent double to close completely upon itself, without manifesting any tendency to crack, even in 1-inch square specimens.

The decrease of ductility is very noticeable in commercial cold-drawing of shafting and wires; but in this case the cold-working is excessive, and therefore it does not follow that with a more moderate degree of cold-working an elastic limit of 70,000 pounds per square inch, associated with a high degree of ductility, can be obtained.

Steel has been cold-worked commercially with the object of improving its elastic properties, as in the case of hoisting cables and cables for suspension-bridges. More often, however, cold-working is primarily resorted to for other purposes. Square reinforcing bars for reinforced concrete beams are cold-twisted for the supposed improvement in their bond properties. Wires and shafting are essentially cold-drawn because of the finished product it furnishes, true to size throughout.

Some tests on fifty reinforced concrete beams, made by the author in connection with this problem, varying in size from 4 inches × 6 inches × (4 feet 6 inches) to 6 inches × 12 inches × (8 feet 0 inches), have shown that when cold-stretched steel is substituted for ordinary mild steel, the strength of a reinforced concrete beam is increased 80 per cent.

In tests on similarly reinforced concrete beams, alternately reinforced with square bars of mild steel and with cold-twisted square bars, the beams reinforced with cold-twisted bars showed an increase of strength of 35 per cent. over the beams similarly reinforced with plain bars, the same percentage of steel being used in both cases.

If a high elastic limit is desired without the true finish associated with cold-drawing, cold-stretching may possibly be resorted to, which can unquestionably be accomplished with a great saving in cost of operation over the cold-drawing process. The pickling of the steel and the maintenance of the dies are totally unnecessary for cold-stretching steel.

Cold-drawing gives a beautifully true product with a somewhat increased elastic limit in torsion, as is manifested by curves K63, Diagram III., and curve 143(v), Diagram VI. However, if a high elastic limit in shear is desired, as for instance in case of shafts, much better results can be obtained by cold-twisting than by cold-drawing, as shown by curves K64, Diagram III., and curve 183(v), Diagram VI. This is true particularly when shafts are used to transmit torque in but one direction. If used to transmit torque in both directions, cold-twisting and tempering still give superior results, as indicated by curve 147 (v), Diagram VI., but in that case the advantage is not so striking. However, it appears that a considerable percentage of modern shafts are designed to transmit torque in one direction only, and because of critical speed considerations the tendency often has been to use as light and flexible shafts as possible. If a light shaft is desired, therefore, as in the case of turbine or aeroplane shafts, may it not be possible to make use of the large increase in torsional elastic limit by cold-twisting, as is illustrated by curves K64, Diagram III., and curve 183(v), Diagram VI. ?

When the perfection of the elastic properties, rather than the general increase of the yield point, is of special importance, it has been shown to be essential that cold-worked steel be tempered at temperatures not much less than that of boiling water.

One manufacturer of helical wire springs related that he was facing bankruptcy because of the large percentage of failures of his springs, until someone suggested to heat the springs in an oven. After heating the springs, which were manufactured of cold-drawn wire stock, they were able to pass the most severe tests for elasticity. Curves 143(v) and 144(v), Diagram VI., which are substantiated by several other tests, clearly show how such tempering perfects the elasticity in torsion of drawn wires.

Lastly, steel balls have been carefully studied with reference to chemical composition and heat treatment. It appears that cold-grinding affects the ultimate strength of steel balls as much as either of the two above-mentioned factors.

Analysis of the Cold-Drawing Process.

The question is asked, "What are the effects of cold-drawing on steel?" It appears that, as far as the elastic properties of the specimen are concerned, the effects of cold-drawing are the same as those due to cold-stretching, and are thus illustrated by the several curves shown in this paper.

In experiments on copper bars, specimens obtained from identically the same stock were tested, hot-rolled, cold-stretched, and commercially cold-drawn. The last two tests gave very similar stress-strain curves.

As regards steel it was not possible to obtain the cold-drawing of pre-tested hot-rolled stock. Therefore, tests were made on cold-drawn steel, the same steel annealed, then this annealed steel cold-stretched and subsequently tested in tension. Again, the stress-strain curves obtained for the commercially cold-drawn steel and the same steel cold-stretched were essentially the same.

Nevertheless, painstaking metallurgical research has been directed towards the effects of cold-drawing on steel, and it has been found, for example, that the surface of a cold-drawn specimen exhibits a greater hardness than the centre, suggesting some essential difference between stretching a bar and cold-drawing a bar through a die.

The following interpretation of the process of cold-drawing is offered, which, considered in the light of what was said earlier in this paper about the effects of cold-working being a function of the cold-working strains and independent of the cold-working stresses involved, points out that the effects of cold-drawing on the elastic properties of steel are essentially the same as those of cold-stretching.

It is well known that straining any material in one direction will produce a corresponding strain in a direction at right angles. Poisson's ratio purports to give the relation between the two strains at right angles to one another.

Bridgman has shown, in discussing the results of his extremely valuable experiments in the Jefferson Laboratory at Harvard University,[1] how a steel bar may be ruptured in the direction of its axis, by means of hydrostatic pressures acting at right angles to its axis only.

---

[1] "Breaking Tests under Hydrostatic Pressure and Conditions of Rupture," *Philosophical Magazine*, July 1912.

In cold-drawing, a bar is forcibly pulled through a die, as indicated by Fig. 1 (p. 128). The stress in the bar, being defined as the load divided by the area, viz. $\frac{P}{A}$, will be somewhat larger at section B–B than at section C–C, because while the load P is essentially the same at both places, the area A_B is slightly smaller at section B–B than its corresponding area A_C at section C–C. We have seen, however, as is most forcibly illustrated by Bridgman, that the elastic limit will be exceeded when a critical strain value is passed regardless of the co-existing stress value.

Although the stress conditions at section C–C may be less severe, the strain conditions at section C–C are the most severe in the bar, because a relatively high stress, $\frac{P}{A_C}$, is accompanied by very high compressive stresses acting normal to the axis of the bar. It has been pointed out how, when a specimen of mild steel is tested in tension and wedge grips are used, the elastic limit is passed, first in the ends of the specimen between the wedge grips, and from there progresses throughout the length of the bar.

In cold-drawing a very similar condition exists. The bar is strained beyond its elastic limit in the portion that is momentarily within the die. Its crystal grains are elongated very similarly to the way they would elongate under pure tension, the bar locally contracts and soon passes on beyond the outside of the die. There the side pressure is removed and the tensile stress $\frac{P}{A}$, without the aid of the normal pressure provided by the walls of the die, proves insufficient to strain the metal any further.

Thus cold-drawing becomes a continuous process. The die is so designed, determined entirely by the practice giving the best results, that the stress in the bar outside of the die is insufficient to permit of plastic flow of metal, while within the die, when the strain resulting from the direct pull is augmented by strains resulting from compression normal to the axis of the bar, plastic flow takes place.[1]

---

[1] For a very interesting and authoritative paper on cold-drawing and its effects, see J. F. Tinsley, *Iron Age*, 1914, p. 1320.

THE EFFECTS OF COLD-WORKING UPON ELASTIC PROPERTIES OF STEEL ARE PERMANENT.

The doubling or even tripling of tensile or torsional elastic properties of steel, if enticing to the man commercially interested in steel, inevitably leads him to inquire into the permanency of these effects. Curves on Diagram IX., stress-strain curves of cold-drawn steel which was aged at least six months and probably many months more, give some idea as to the permanency of the effects of cold-working upon steel. They manifest a perfect and high elastic range. Incidentally, they show how the elastic limit of steel is inevitably reduced to its original value upon heating it above the critical temperature and allowing it to cool in air. Possibly the most emphatic argument for the permanency of the beneficial effects of cold-working steel is found in the continued use of cold-worked steel during generations. It is stated that the Brooklyn bridge, constructed in 1872, made almost throughout of cold-drawn wires, is permitted to be stressed at present at least to double the stresses for which it was designed, based upon the reports of various technical commissions. Cold-rolled shafting has been used for a great many years, and helical springs are preferably made of cold-drawn wire. Never, in such cases, has a loss of elastic properties been noticed with time. Although the merits of the square twisted reinforcing bar is a matter under dispute, it is never even intimated that its elastic properties may be deleteriously affected with time.

In conclusion, the author desires to express his appreciation of the advice and encouragement received from Professor W. C. Hoad and Professor Edward D. Campbell of the University of Michigan, in carrying out his investigations, as well as his indebtedness to Mr. L. S. Cope, Metallurgist of the Hoover Steel Ball Company of Ann Arbor, Michigan, for the preparation of micrographs Nos. 1, 2, and 3, and for his liberal supplies of steel balls for the ball tests.

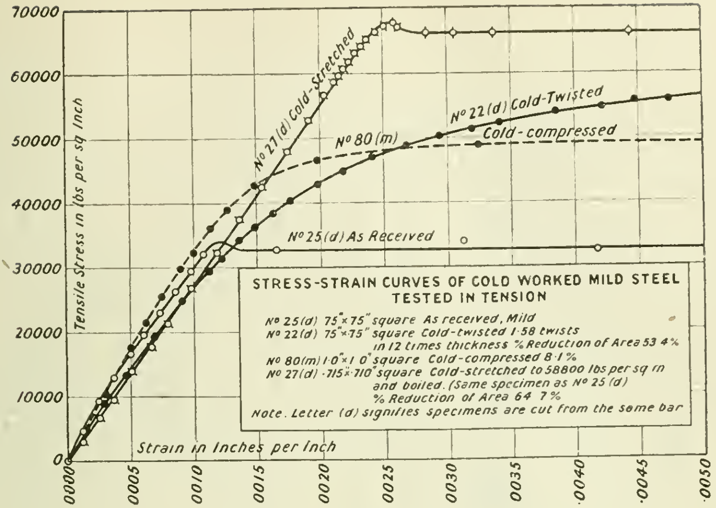


DIAGRAM I.

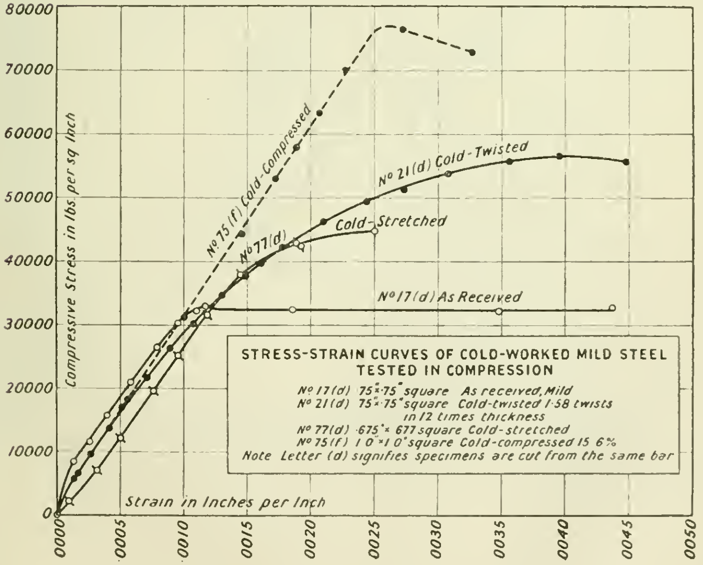


DIAGRAM II.

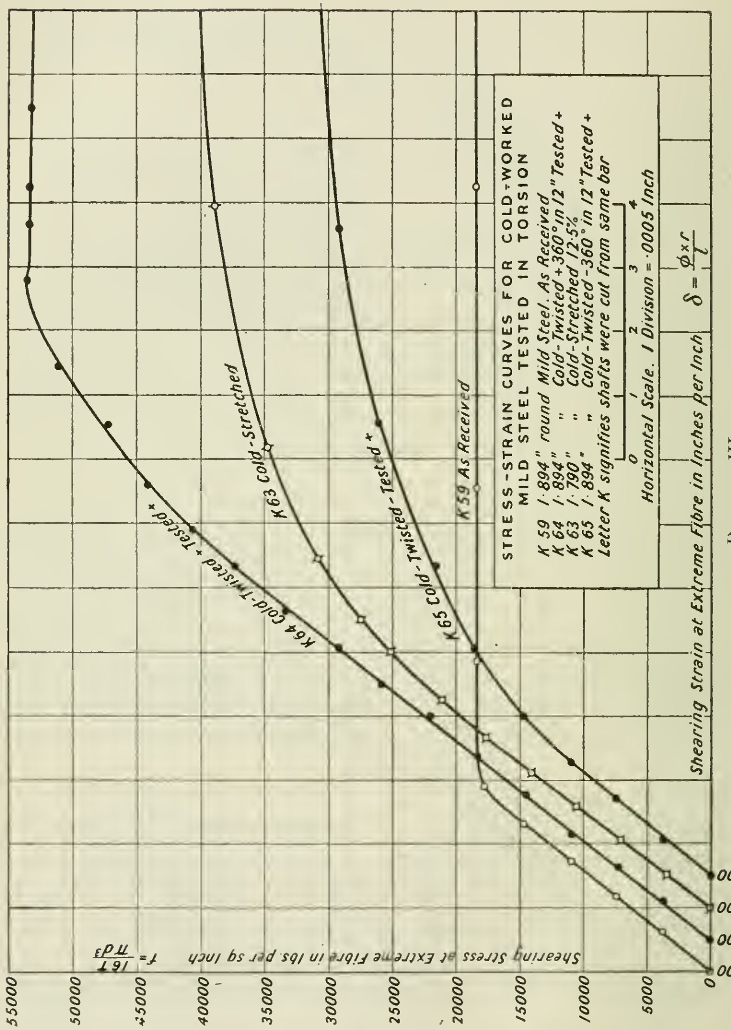
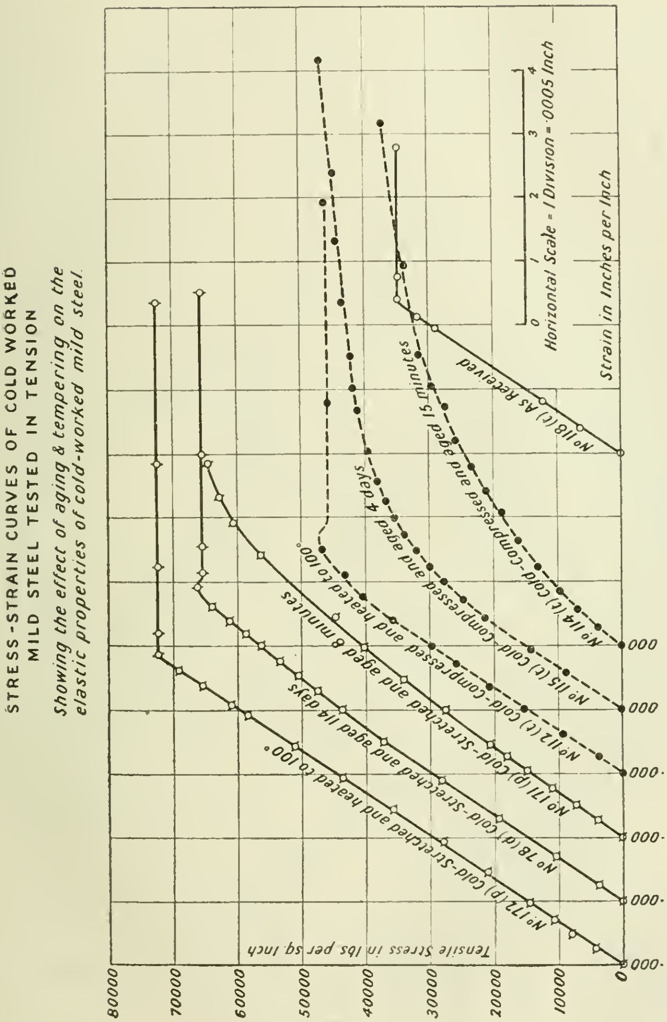

STRESS-STRAIN CURVES FOR COLD-WORKED MILD STEEL TESTED IN TORSION
K 59 1·894" round Mild Steel. As Received
K 64 1·894" " Cold-Twisted +360° in 12" Tested +
K 63 1·790" " Cold-Stretched 12·5%
K 65 1·894" " Cold-Twisted -360° in 12" Tested +
Letter K signifies shafts were cut from same bar
0 1 2 3 4
Horizontal Scale. 1 Division = ·0005 Inch
$\delta = \frac{\phi \times r}{l}$
Shearing Strain at Extreme Fibre in Inches per Inch
Shearing Stress at Extreme Fibre in lbs. per sq inch $f = \frac{16T}{\pi d^3}$
K64 Cold-Twisted + Tested +
K63 Cold-Stretched
K65 Cold-Twisted - Tested +
K59 As Received
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
000
000
000
000

DIAGRAM III.



STRESS-STRAIN CURVES OF COLD WORKED MILD STEEL TESTED IN TENSION

Showing the effect of aging & tempering on the elastic properties of cold-worked mild steel.

DIAGRAM IV.

STRESS-STRAIN CURVES OF COLD-WORKED MILD STEEL TESTED IN COMPRESSION

Showing the effect of aging & tempering on the elastic properties of cold-worked mild steel.

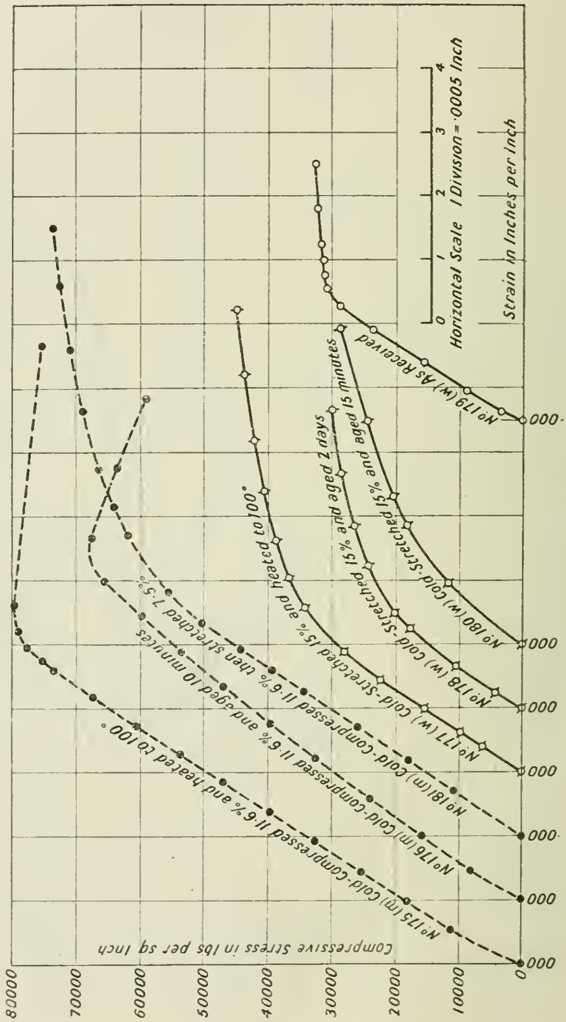


DIAGRAM V.

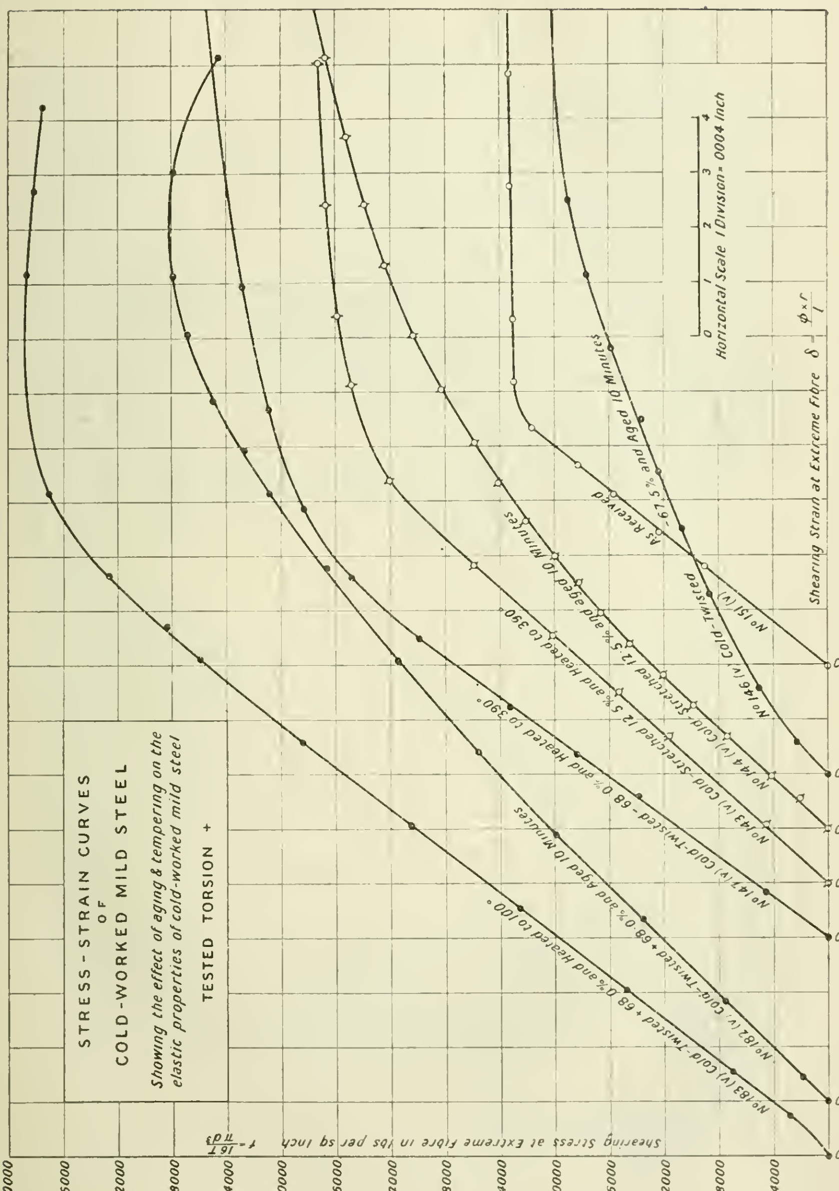

STRESS-STRAIN CURVES
OF
COLD-WORKED MILD STEEL
Showing the effect of aging & tempering on the elastic properties of cold-worked mild steel
TESTED TORSION +
No 183 (v) Cold-Twisted + 68.0% and Heated to 100°
No 182 (v) Cold-Twisted + 68.0% and Aged 10 Minutes
No 147 (v) Cold-Twisted - 68.0% and Heated to 390°
No 143 (v) Cold-Stretched 12.5% and Heated to 390°
No 144 (v) Cold-Stretched 12.5% and Aged 10 Minutes
No 146 (v) Cold-Twisted - 67.5% and Aged 10 Minutes
No 151 (v) As Received
000
0 1 2 3 4
Horizontal Scale 1 Division = .0004 Inch
Shearing Strain at Extreme Fibre $\delta = \frac{\phi \times r}{l}$
Shearing Stress at Extreme Fibre in lbs per sq inch $f = \frac{16T}{\pi d^3}$
60000
56000
52000
48000
44000
40000
36000
32000
28000
24000
20000
16000
12000
8000
4000

DIAGRAM VI.

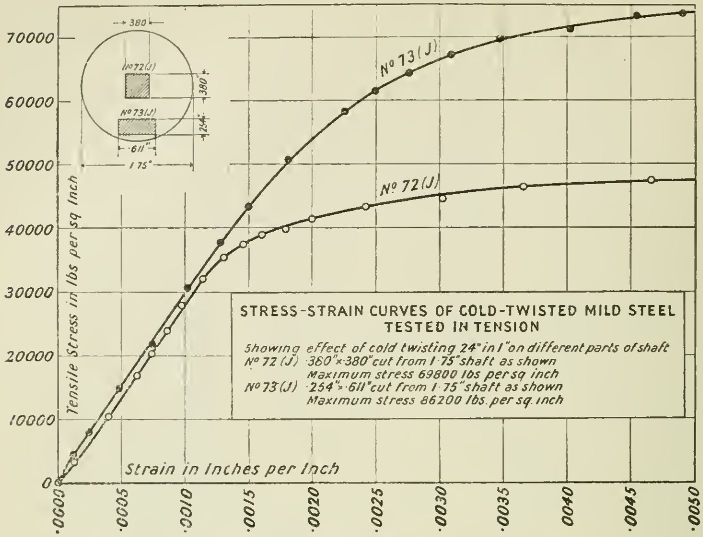


Diagram VII.

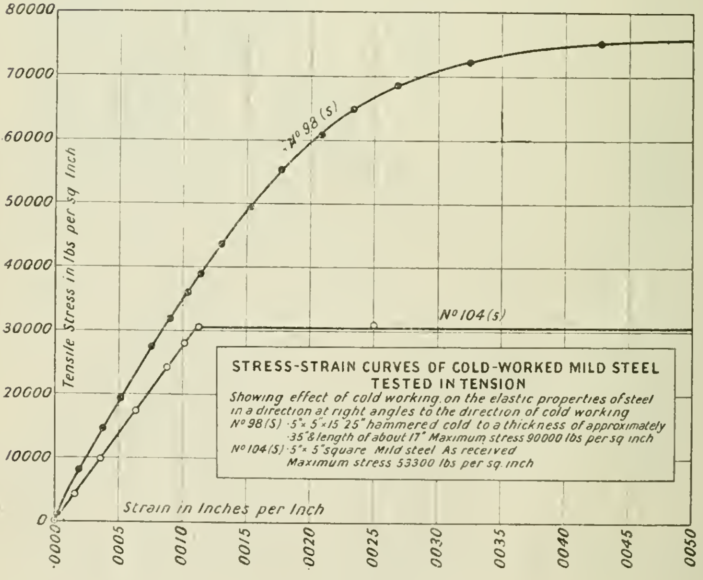


Diagram VIII.

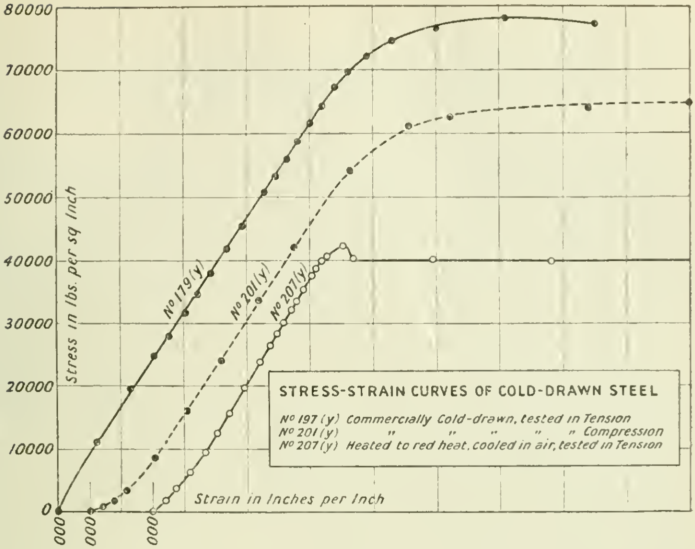

80000
70000
60000
50000
40000
30000
20000
10000
0
Stress in lbs. per sq Inch
Nº 179 (y)
Nº 201 (y)
Nº 207 (y)
STRESS-STRAIN CURVES OF COLD-DRAWN STEEL
Nº 197 (y) Commercially Cold-drawn, tested in Tension
Nº 201 (y) " " " " " Compression
Nº 207 (y) Heated to red heat, cooled in air, tested in Tension
Strain in Inches per Inch
000
000
000

DIAGRAM IX.

DISCUSSION AND CORRESPONDENCE ON MR. VAN DEN BROEK'S REPORT.[1]

Colonel N. T. **Belaiew**, C.B. (London), wrote, drawing attention to the author's suggestion that changes in elastic properties of steel were determined by the degree and kind of deformation given to the specimen in the process of cold-working. With reference to that point the watering of Oriental blades was, in his opinion, of the highest interest. That watering showed the amount of mechanical treatment to which the article had been subjected, as it changed from parallel stripes to wavy ones, then to mottled and finally to vertebræ, forming great grape-vine patterns which extended over the whole breadth of the bar and divided it into almost even and equally patterned sections. The last watering showed the maximum of deformation on the one hand, and the maximum of mechanical qualities on the other.

It was true that, generally speaking, the damascene blades were forged after a certain heating of the article, only observing the utmost precaution not to exceed the critical temperature. But, as Anossoff pointed out and fully endorsed by his own practical experience, in many cases no heating was necessary, and the articles were cold-worked in the strictest sense of the word.

Mr. C. H. **Ridsdale** (Middlesbrough) wrote that the author had said, " When steel is strained and crystals begin to break up, one crystal which fails diverts more stress to its neighbour, this adjoining crystal breaks and in turn causes the next one to break, provided the stresses are kept constant." That was exactly what took place when steel cracked in cold-shearing. He (Mr. Ridsdale) had collected and examined hundreds of specimens over many years, and in almost every case the crack ran from the starting-point, not simply along crystal boundaries, but straight on through the mass of the crystalline grains themselves, only taking a boundary if it happened to be in line.

After a very careful study of the subject, he had come to the conclusion that those cracks in most cases started instantly the pressure of the blade had forced the portion being cut off to commence to part from the rest, and that they were caused by the sudden " rebound " when the steel was released from the state of maximum compression, and further that they started from that point—which was generally from midway to two-thirds down the billet. Similarly on knocking a close-double cold-bend flat, one could sometimes see the spring back and hear the crack. He could not now give all the evidence, but he hoped to publish it later. He was convinced that in the majority of instances cold-shearing cracks, and those resulting from similar conditions, were not (within limits) a question of composition or impurity—for those might vary within a considerable range without producing failure—but were entirely a function of stresses and strains, dependent on the relation between the size of piece and power and speed of shears, condition and play of blades, &c.—in short, the rate at which the force was applied as compared with the strength and resistance of the piece. The author likewise stated: "When the machine is stopped after the yield-point of the specimen is passed the crystals keep on rupturing for a short time. . . ."

---

[1] The Report by Mr. Van Den Broek was presented at the May 1918 Meeting of the Iron and Steel Institute, and was the subject of the discussion and correspondence printed above. [Note by Editor.]

In that connection he might remind members that it was not uncommon for a billet which had been cold-sheared and showed a perfectly clean cut to crack some time after; and, for instance, pieces might be seen and heard to crack several minutes or even *an hour* or more after shearing was completed. As regarded bright cold-drawn shafting: transverse cracks, which rendered it extremely brittle—so much so that it might break in pieces when dropped a few feet—were sometimes met with, especially in the larger sizes, say over 1 inch diameter. They might be so small as to be invisible, except under magnification or on etching. Sometimes no doubt they were entirely due to the stresses being concentrated locally, till at that point they exceeded the elastic limit of the material, resulting in its rupture. That would be better understood when it was borne in mind that the rounds before drawing were not true. To illustrate that, he had had lengths centred and a small spiral groove turned on the parts that stood up until the tool only just touched the surface at the lowest part, the higher parts being of course cut to the depth by which they exceeded the normal diameter.

On a 2-inch diameter bar, that cut would perhaps run from nothing to $\frac{3}{32}$ inch deep, and as the bar had to leave the die round, vastly greater strains would be concentrated on, and much greater flow have to take place from those parts which stood up. But transverse cracks were not always tears resulting from stresses. They were also due to seizing arising from want of lubrication locally, and no doubt as a concomitant, heat arising therefrom. Indeed in some cases that was so to such an extent that they were really thermal cracks similar to those produced in rail-heads by the slip of the driving-wheel, or by skidding of the wheels. He had met with specimens both of round and flat or angular cold-drawn rods, which on fracturing showed the purple tint on the outer edges, passing as the crack penetrated, through all the shades, brown, straw, &c., down to colourless, which were sometimes found in rail-heads fractured through thermal cracks. The author also mentioned that "a steel bar may be ruptured in the direction of its axis by means of pressures acting at right angles to its axis only."

He (Mr. Ridsdale) had seen a number of instances of that, the bars having split longitudinally about midway of their diameter, the crack going sometimes right across and sometimes part way, but readily splitting right across when struck. He regarded that as another manifestation of the same fault, viz. when the want of truth from round, instead of fluctuating from side to side with some regularity, was chiefly along one side, the bar being slightly oval, and so, when drawn, there being more extension of one-half than another tending to rupture along the centre line where the stresses met, splitting and creep occurred. Sometimes the bright fractured surface showed a distinct rubbed effect where one-half had slidden over the other. All these cold-drawn bars were of material which was quite soft chemically and mechanically, and only showed brittleness at the cracked and strained parts.

As regarded the point that cold-working did "not affect in any way the electric resistivity of the steel" (p. 22), it was extremely interesting to find that what he had himself found[1] for steel worked at from 800° C. to 600° C. held good also down to ordinary atmospheric temperatures, and helped to complete the available data.

With respect to effects of cold-working being permanent, he had in 1898 cited instances where the steel had been worked till brittle, and had exhibited a piece of steel worked at blue heat which was just as brittle on retesting at the end of ten years; whilst a common instance where the beneficial effects were retained, that with "cold-rolled springs—never had a loss of elastic properties been noticed with time," he cited the instance of the top of a pendulum (cold-rolled or drawn down to ribbon) of a grandfather's clock, where a rod of soft iron was endowed with spring-like properties and retained its resilience after 80 or 100 years regular work.

Dr. W. ROSENHAIN, F.R.S. (National Physical Laboratory, Teddington), was sorry to say, with regard to Mr. Van Den Broek's paper, that he had to take up a sceptical attitude. He thought the experimental method used by Mr. Van Den Broek was inadequate and unsuited to the purpose. Instead of a strain gauge reading to 1/10,000th inch, it was necessary for researches of that kind to employ an instrument of the sensitiveness of the mirror extensometer, with a sensitiveness of 1/250,000 inch. What Mr. Van Den Broek had done was to base conclusions on measurements with his instrument and endeavour thereby to upset the conclusions well established by other workers using much more sensitive and more reliable methods. Anyone reading Bauschinger's remarks quoted in the paper could not fail to put upon them the opposite interpretation to that which Mr. Van Den Broek had done. Bauschinger made it quite plain that he regarded his data as showing that the elastic limit in compression was lowered by over-strain in tension and *vice versâ.* Furthermore, there was a piece of work, which he thought was probably the most conclusive that had yet been done on the subject, by Bairstow at the National Physical Laboratory, and published in a paper in which he confirmed Bauschinger's view of the constancy of the total elastic range very fully and accurately. It would take a great deal more evidence and much more accurate work than Mr. Van Den Broek's paper showed to shake that conclusion in the very least degree. It would have suited him, in regard to his own personal views, very much better if it were not so. As the author of the paper said, this point constituted one of the most serious difficulties in the amorphous theory of hardening by strain, of which he was an advocate, and he would have been only too pleased to accept Mr. Van Den Broek's conclusions if he felt they were soundly based. He would warn readers of the paper not to accept Mr. Van Den Broek's account of the amorphous theory as representing his (Dr. Rosenhain's) views or those of his colleagues who had been working on the subject, as it was not a thoroughly satisfactory statement. The practical conclusions of the paper were to some extent invalidated if the results could not be relied upon, but none the less there was a good deal of truth in them, as it had always been realised that the raising of the elastic limit by cold work had its value under certain conditions and for certain purposes. Everyone was accustomed to the use of cold-drawn wire, and a great many things would be almost impossible if cold-drawn wire with its high elastic limit were not available. He did not think that anyone had attempted to suggest that the mere efflux of time, leaving the material more or less under static conditions, would affect the elastic limit of cold-worked steel. What was said and what he thought had been proved was that when the elastic limit of steel had been raised in that way, if the steel were subjected to alternating stresses, that high elastic limit became entirely fictitious. It had been shown over and over again by careful alternating stress tests that cold worked material was not one whit better, but if anything a little worse, under alternating stresses, than the same material in the annealed condition. Therefore if a structure were exposed to alternating stresses it was idle to rely on the raised elastic limit obtained by cold-work. With that reservation, the practical conclusions might with safety be accepted as to the value of cold-worked material, but that limitation was vital and necessary.

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[1] *Journal of the Iron and Steel Institute*, 1917, No. II. p. 263.

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Carnegie Scholarship Memoirs, 1920.]

Iron and Steel Institute.

THE EFFECT OF FLUORSPAR ADDITIONS ON THE PHOSPHATES IN BASIC SLAG.*

BY F. BAINBRIDGE (SALTBURN).

PART I.

THE MANURIAL VALUE OF BASIC SLAG CONTAINING FLUORSPAR.

WHEN the author applied for the "Carnegie Research Grant," it was not his intention at the time to deal with the above subject from the agricultural standpoint; but after consultation with, and at the suggestion of, Dr. J. E. Stead (Middlesbrough) it was decided to carry out a series of experiments, with a view to supplementing the data already in the hands of the agricultural chemists.

Dr. E. J. Russell (Rothamstead Experimental Station) was informed of the author's intention, and immediately forwarded the necessary details with reference to arrangement of crops and feeding of same during growth.

Preparations were made to carry out experiments to show the effect of a citric-insoluble slag on the growth of barley, compared with a series of plants treated with a soluble slag and also a series without any slag, with a view to ascertaining whether the processes now adopted by basic open-hearth steel plant managers tend to improve or injure the manurial value of basic slag.

Arrangement of Experiments.—After considerable delay, owing to difficulty in obtaining the necessary pots, the experiments were started on March 21, 1918.

Ground.—A suitable site was selected in the open, and not shaded from the sun, and a piece of ground 30 feet square fenced in with corrugated sheeting 7 feet high so arranged as to permit of the sheets being lowered during the fine weather, the inside also being painted white in order to allow a maximum of light.

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* Report received March 5, 1919.

Inside the sheeted enclosure, and occupying the centre space, was fixed a wire-netted enclosure, 15 feet by 15 feet, to protect the crop from birds, &c.

Materials Used.—As it was essential to have the different slags to be used as similar in composition as possible, the management of the Skinningrove Iron Company arranged that one of their basic open-hearth steel furnaces should be worked as free as possible from fluorspar, and when ready for removal of slag the furnace was tilted and about 4 cwt. of slag run off into a small pan, the furnace put level again, and about 2 tons of fluorspar added. The spar was allowed twenty minutes to work through the bath, and then a second pan run off.

On analysis, the two slags gave the following results:

	No. 1 Slag (without Fluorspar).	No. 2 Slag (with Fluorspar).
	Per Cent.	Per Cent.
Silica	11·20	10·20
Ferrous oxide	14·79	16·07
Ferric oxide	7·00	5·86
Alumina	7·89	7·99
Phosphoric acid	14·48	14·10
Manganous oxide	0·37	0·37
Calcium oxide	39·10	39·90
Magnesium oxide	5·07	4·53
Total iron	16·40	16·60
Soluble P_2O_5 (2 per cent. citric acid)	10·50	0·874
Percentage of total P_2O_5 soluble	72·51	6·2

In addition to the above a third slag was supplied by Messrs. Alexander Cross & Sons, which had the following analysis:

	Per Cent.
Total phosphoric acid	14·32
Soluble phosphoric acid	11·685
Percentage of total P_2O_5 soluble	81·60

The analyses of the other fertilising constituents were as follows:

Sodium nitrate containing 95 per cent. $NaNO_3$.
Potassium sulphate containing 98 per cent. K_2SO_4.
Magnesium sulphate containing 49 per cent. $MgSO_4$.*
Calcium carbonate added in the sand.

In order that the tests might be strictly comparable, it was necessary to select a soil as free from phosphoric acid as possible; Kirkleatham blown sand being finally selected for the purpose.

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* The remainder being water of crystallisation.

The sand contained 4·8 per cent. of calcium oxide existing as carbonate, and 0·024 per cent. phosphoric acid soluble in strong hydrochloric acid.

The pots used in the experiment were 15 inches deep by 12 inches in diameter (internal), and glazed both inside and out.

The barley seed used was supplied by the Rothamsted Experimental Station.

Preparation of the Pots.—The experiment was divided into four series:

No. 1 consisting of 4 pots without any slag, numbered 1 to 4.
,, 2 ,, 4 ,, containing insoluble slag, Nos. 5 to 8.
,, 3 ,, 4 ,, ,, Skinningrove 72·5 per cent. soluble slag, Nos. 9 to 12.
,, 4 ,, 4 ,, ,, Cross 81·6 per cent. soluble slag, Nos. 13 to 16.

The pots were to be supplied with the following plant food, based on the total weight of sand used:

2	per cent.	carbonate of calcium (already in the sand).
0·05	,,	total phosphoric acid (in form of slag).
0·05	,,	potassium sulphate.
0·05	,,	magnesium sulphate.
0·10	,,	sodium nitrate.

Of the above plant food, all the slag, half the potassium sulphate, a quarter of the sodium nitrate, and all the magnesium sulphate were intimately mixed with the top 6 inches of sand in each pot.

The pots were filled with the following mixtures:

Sand	All series	70 lb. (31·818 kilos) per pot.
Basic slag	Series I.	No slag.
	Series II.	112·83 grammes insoluble fluoride slag.
	Series III.	109·87 ,, Skinningrove soluble slag.
	Series IV.	111·10 ,, Cross soluble slag.
Potassium sulphate (98 per cent.), all series		8·115 grammes
Sodium nitrate (95 per cent.), all series		8·373 ,,
Magnesium sulphate (49 per cent.), all series		32·45 ,,

A solution was made of the remaining 8·115 grammes potassium sulphate and 25·117 grammes sodium nitrate, which solution was watered into the sand in each pot as the experiment progressed, the whole being added before the plants were half-grown.

Progress of the Experiment.—On March 21, 1918, the filled pots were placed in the wire enclosure in the order shown in Fig. 1, and remained exposed to the atmosphere until April 2, on which date ten barley seeds were planted exactly 1½ inches deep in pairs equally round each pot, as shown in Fig. 2, and 1 litre of water added, after which the sand was kept moist throughout the period of growth by additions at intervals, the same quantity of water being added to each pot, the amount being regulated by the least moist series at each application.

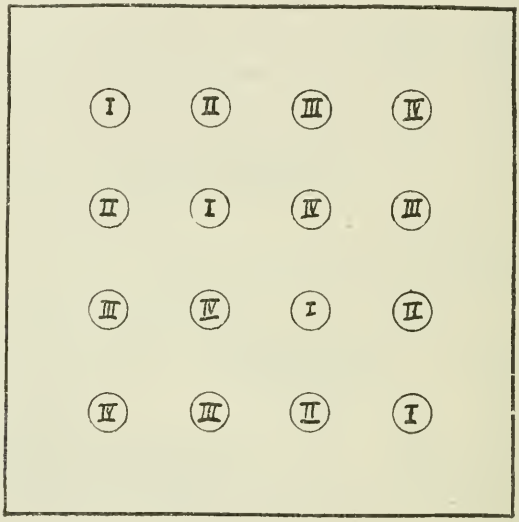

Fig. 1.

On April 30 the seedlings were an average of 1¼ inches high, and sufficient were removed to leave five seedlings in each pot.

Unfortunately three seedlings failed to mature, leaving only four roots each in pots Nos. 3, 13, and 14, the first being in Series I. and the two latter in Series IV.

On June 28, 1918, the photographs shown in Figs. 3, 4, 5, and 6 were taken, and it was noted at this period that :

In Series I. only single shoots per seed were visible.

Series II. showed an average of three shoots per seed, and Series III. and IV. showed five to six shoots per seed, the height of the shoots in Series II., III., and IV. being about the same.

On August 13 the crops were nearly matured, and the photographs shown in Figs. 7, 8, 9, and 10 were taken.

In Series I. no barley heads were visible.

Series II. showed a much greater length of straw than Series III.

Series III. and IV. appeared to be in close agreement with each other, and although the stalks were about a foot shorter than Series II., the yield of grain could be seen to be considerably greater, owing to the increase in the number of barley-bearing heads per seed planted, compared with the increase in Series II.

On August 24 it was noticed that in several of the pots the seed was commencing to leave the straw, owing to the high winds prevailing at this period, although several smaller heads of barley were still somewhat green.

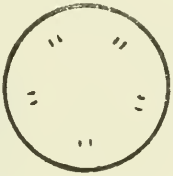

Fig. 2.

It was at first thought the best policy would be to cut the ripe heads off and allow the remainder to mature, but, on referring the matter to Dr. Russell, it was decided to cut the whole crop at the same time, and this operation was carried out on August 31.

The heavy rains which have since prevailed in this district have proved the wisdom of the latter consideration.

The straw and grain from each pot were dried on trays in the sun with constant turning, and then thrashed and weighed.

At the time of cutting, the difference in colour of the straw and the length of the top internodes in each series were particularly noticeable.

Series I. showed a reddish crimson colour.

Series II. a deep reddish crimson, which was also apparent on the grain in the form of dark red lines.

Series III. and IV. showed no sign of crimson, the straw and grain being a good golden yellow.

On measuring the length of the top internodes of the straw, Series II. showed an average length of 10·53 inches as compared with an average of 7·5 inches in the case of Series III.

Fig. 11 (Plate III.) gives some idea of these differences.

The weights of the crop on September 19 were as follows:

Series No.	Pot No.	Weight of Air-dried Grain.	Weight of Air-dried Straw.
		Grammes.	Grammes.
I.	1	nil	1·80
	2	nil	2·30
	3	nil	3·05 *
	4	nil	4·05
	Average per pot	nil	2·80
II.	5	45·134	78·35
	6	41·936	78·55
	7	44·509	72·25
	8	43·150	70·50
	Average per pot	43·682	74·91
III.	9	71·204	80·35
	10	68·775	78·40
	11	74·371	85·95
	12	70·360	82·50
	Average per pot	71·177	81·80
IV.	13	62·721	77·90[1]
	14	54·649	67·00[1]
	15	67·228	76·60
	16	71·146	70·65
	Average per pot	63·936	73·04

The total weights of the crop in Series I. to IV. have been plotted in Fig. 12, the height of each column being proportional to the weight of straw and grain in each series, and Fig. 13 shows the difference in bulk of grain in the different series.

The air-dried straw and grain were submitted to Dr. Russell, who very kindly agreed to estimate the total phosphoric acid in the ash remaining, after combustion of the dry matter in each series, with the following interesting results:

---

* Four plants only instead of five. It has been shown at the Rothamstead Experimental Station that the number of plants per pot does not materially affect the total yield.

	Weight taken.*	Dry Matter.	Ash.	P_2O_5 in Ash.	P_2O_5 in Sample.
	Grammes.	Grammes.	Grammes.	Per Cent.	Grammes.
Series I.					
Pots 1, 2, 3, 4	8·5	7·3	0·83	1·77	0·015
Series II.					
Pots 5, 6, 7, 8. Grain .	162·5	139·1	3·70	19·43	0·719
Straw	253·2	210·5	18·35	0·604	0·111
Ears	17·5	15·4	1·25	1·58	0·020
Series III.					
Pots 9, 10, 11, 12. Grain .	271·5	232·1	7·72	33·4	2·579
Straw	279·7	229·6	21·75	3·31	0·720
Ears	32·9	28·6	2·50	5·88	0·147
Series IV.					
Pots 13, 14, 15, 16. Grain	247·5	211·4	6·70	33·2	2·222
Straw	243·8	208·0	19·10	2·53	0·483
Ears	27·5	23·9	2·12	4·42	0·094

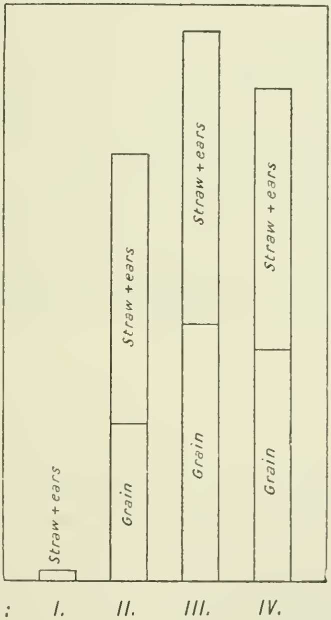

FIG. 12.

Summary.

	Total Dry Matter.	Total P_2O_5 in Ash.
Series I. No slag	7·3	0·015
,, II. Insoluble slag	365·0	0·850
,, III. Skinningrove soluble slag . . .	490·3	3·446
,, IV. Bought soluble slag	443·3	2·799

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* The weight taken consists of the total yield of grain, straw, and ears, and is lower than the previous list of yield weights, owing to the samples drying considerably by exposure after being weighed, and before being submitted to Dr. Russell for analysis.

Deductions.

Taking the yield of Series III. as 100 per cent. we have—

	Yield of Grain. Per Cent.	Yield of Straw. Per Cent.
Series I.	nil	3·42
„ II.	61·37	91·57
„ III.	100·00	100·00

and, assuming that the 100 per cent. yield is strictly proportional to the solubility, we would only expect a yield of 8·5 per cent. for Series II. But as the actual result is far in excess of this amount, it must be concluded that the solubility of two slags is not a correct indication of their relative fertilising value.

The length of top internode of the straw in Series II., together with the colour of the straw, would point to phosphate starvation, as both these conditions have been repeatedly obtained in cases of deliberate phosphate starvation (Dr. Russell). The result of the ash determinations would point to an increased feeding value for corn grown with soluble phosphoric slag.

It is the author's intention to carry out a further series of experiments during the coming season, in order to determine whether the addition of insoluble phosphate to the soil in November will increase its value as a fertiliser if exposed to the atmosphere during the winter months.

Summary.

1. When a basic slag made with addition of large amounts of fluorspar is used for manurial purposes, and is applied just before the seed is sown in the spring of the year, the crop is not as good as when a more soluble slag is applied at the same time and in the same proportion with regard to total phosphoric acid.

2. A basic slag made with the addition of fluorspar has considerable fertilising value notwithstanding its low solubility.

3. When barley is grown in soil treated with a citric-soluble phosphoric slag, the phosphoric acid content of the grain and straw produced is much greater than when a phosphoric slag made with large additions of fluorspar is applied, under similar conditions.

PART II.[*]

THE MANURIAL VALUE OF BASIC SLAG CONTAINING FLUORSPAR (*continued*).

THE results obtained in Part I. of this memoir indicated the possibility of increasing the fertilising value of an insoluble phosphate by adding it to the soil in late autumn, and thus exposing it to the atmosphere during the winter months, and the following note gives the details and results of the experiments carried out in this connection.

Arrangement of Experiments.—Experiments were commenced on November 11, 1918.

Ground and Fittings.—The same enclosure and ground were used as in the previous experiments.

Materials Used.—Slags Nos. 1 and 2, the analyses of which are given on p. 2, Part I., of this memoir, together with a third basic open-hearth slag, provided by the Skinningrove Iron Co., Ltd., of the following analysis :

	Per Cent.
Total phosphoric acid	12·74
Soluble phosphoric acid (2 per cent. citric acid) . .	3·32
Percentage of total P_2O_5 soluble	26·06

The other fertilising constituents used, namely, sodium nitrate, potassium sulphate, and magnesium sulphate, were of the same composition as in the previous experiments. The sand and pots were also similar. The barley seed used was supplied by the Rothamstead Experimental Station.

Preparation of the Pots.—The trial was divided into five series :

No. 1 consisting of 4 pots without any slag, numbered 1 to 4.
No. 2 ,, 4 ,, containing insoluble slag, Nos. 5 to 8.
No. 3 ,, 4 ,, ,, Skinningrove 72·5 per cent. soluble slag, Nos. 9 to 12.
No. 4 ,, 3 ,, ,, Skinningrove 26·06 per cent. soluble slag, Nos. 13 to 15.
No. 5 ,, 3 ,, ,, Skinningrove 72·5 per cent. soluble slag, Nos. 16 to 18.

The pots were supplied with the same percentage plant food, based on total weight of sand used, as in Part I.

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[*] Report received April 8, 1920.

The pots were filled with the following mixtures:

Sand . .	All series,	70 lbs. (31·818 kilos) per pot.
Basic slag .	Series I.	No slag.
	Series II.	112·83 grammes insoluble fluoride slag.
	Series III.	109·87 ,, Skinningrove soluble slag.
	Series IV.	124·90 ,, ,, 26·06 per cent. soluble slag.
	Series V.	109·87 ,, ,, soluble slag.
Potassium sulphate (98 per cent.), all series . . .		8·115 grammes
Sodium nitrate (95 per cent.), all series		8·373 ,,
Magnesium sulphate (49 per cent.), all series . . .		32·45 ,,

A solution was made of the remaining 8·115 grammes potassium sulphate and 25·117 grammes sodium nitrate, which solution was watered into the sand in each pot as the experiment progressed, the whole being added before the plants were half-grown.

Progress of the Experiment.—On November 11, 1918, the pots forming Series I., II., and III. were filled with the necessary mixtures and placed in the wire enclosure, the drainage hole at the base of each pot being connected by a good rubber stopper and glass tubing to a glass flask sunk below the level of the ground. No moisture additions were made other than the natural rainfall, the surplus water draining off from each pot being collected, stored, and finally watered in again as the pots dried.

The three series mentioned above were allowed to stand until April 5, 1919, on which date the pots in Series IV. and V. were filled with their respective mixtures, 1 litre of water added to each pot in Series IV. and V., and ten barley seeds planted exactly 1½ inches deep in pairs round each pot throughout all the series.

The bottles and connections were removed from the drainage holes in Series I., II., and III., and solid rubber stoppers placed in the drainage holes of all the pots.

From this point the experiment proceeded exactly as in the case of that recorded in Part I.

On April 26, 1919, the seedlings in Series I., II., and III., were an average of 2½ inches high, and those in Series IV. and V. about 1½ inches high.

Sufficient seedlings were removed to leave five in each pot. Unfortunately, whilst drying the cut crop of Series V., a very large proportion of the grain and straw was destroyed by mice during the author's absence, and therefore no strict comparison can be drawn between the fertilising value of a 72·5 per cent.

soluble slag and a 26 per cent. soluble slag when the slag is applied just before the seed is sown in the spring of the year.

On this account no further reference is made to Series V.

On September 1, 1919, photographs were taken. They showed, in Series I., a very considerable increase over the previous year, whereas Series III. was not so good. The crop was cut on September 2, 1919, all the plants being fully matured. At the time of cutting the difference in the colour of the straw was again noticeable as in the previous year.

Series I. showed a reddish crimson colour.

Series II. showed some quantity of reddish crimson, although not so much as in the previous year.

Series III. was a good golden yellow.

Series IV. showed principally golden yellow with signs of the reddish crimson here and there.

The straw and grain from each pot was dried in the sun with constant turning, then thrashed and weighed.

The weights of the crop on September 26th were as follows :

Series Number.	Pot Number.	Weight of Air-dried Grain.	Weight of Air-dried Straw.
		Grammes.	Grammes.
I.	1	8·62	28·20
	2	5·57	24·00
	3	15·04	27·40
	4	3·70	26·10
	Average per pot	8·23	26·42
II.	5	43·27	80·70
	6	46·17	75·00
	7	42·50	67·50
	8	44·25	75·30
	Average per pot	44·05	74·62
III.	9	62·70	83·20
	10	59·11	84·50
	11	53·06	80·20
	12	55·34	80·40
	Average per pot	57·55	82·07
IV.	13	46·30	72·20
	14	39·63	84·70
	15	40·80	81·00
	Average per pot	42·24	79·30

The total weights of the crop in Series I. to IV. have been plotted in Fig. 13, the height of each column being proportional to the weight of straw and grain in each series.

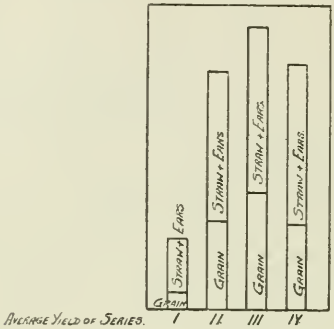

Fig. 13.

Dr. E. J. Russell (Rothamstead) very kindly agreed to estimate the total phosphoric acid in the ash remaining, after combustion of the air-dried straw and grain, with the following results :

Series.	Weight of Grain.	Weight of Dry Matter.	Ash in Dry Matter.	P_2O_5 in Ash.	P_2O_5 in Dry Matter.	Total P_2O_5.
	Grammes.	Grammes.	Per Cent.	Per Cent.	Per Cent.	Grammes.
				Grain.		
I. Without slag .	8·23	7·78	3·34	13·10	0·437	0·034
II. Insoluble slag .	44·05	41·77	3·59	16·70	0·599	0·250
III. Soluble slag .	57·55	54·60	3·50	30·10	1·054	0·576
IV. 26 per cent. soluble slag .	42·24	39·67	3·30	26·80	0·885	0·351
				Straw.		
I. Without slag .	26·42	18·90	8·20	2·39	0·196	0·037
II. Insoluble slag .	74·62	62·00	9·76	0·77	0·075	0·046
III. Soluble slag .	82·07	64·80	10·18	1·97	0·201	0·130
IV. 26 per cent. soluble slag .	79·30	56·20	11·89	1·38	0·164	0·093

Summary.

	Total Dry Matter.	Total P_2O_5.
	Grammes.	Grammes.
Series I.	26·7	0·071
,, II.	103·8	0·296
,, III.	119·4	0·706
,, IV.	95·9	0·444

Deductions.

As in the previous year's experiments, we find that the yield from the insoluble slag is far in excess of that which the solubility value would lead us to expect if we assumed that the yield were strictly proportional to the solubility.

The colour of the straw indicates phosphate starvation in the case of Series I. and II., as was similarly indicated in the previous experiments.

The ash determinations show a considerably larger uptake of phosphoric acid from the soluble slag than from the insoluble slag.

More has been taken from Series III., weathered over the winter, than from Series IV.

The insoluble slag has not been entirely ineffective: it has given satisfactory yields both of grain and straw, but it fails to increase the phosphoric acid contents of the grain and straw as much as the soluble slag does, and therefore gives a product of probably less feeding value.

Summary.

1. When a basic slag made with addition of large amounts of fluorspar is used for manurial purposes, and is applied in the late autumn, the proportionate yield compared with the yield of a soluble slag is better than when the same slags are applied just before the seed is sown in the spring of the year.

2. A basic slag made with addition of fluorspar has considerable fertilising value, notwithstanding its low solubility confirming deduction (2), Part I.

3. Confirmation of deduction (3), Part I.—the results demonstrating the value of soluble slag as a plant nutrient.

PART III.*

THE NATURE AND SOLUBILITY OF THE PHOSPHATES CONTAINED IN BASIC OPEN-HEARTH SLAG MADE WITH ADDITIONS OF FLUORSPAR.

Introductory Note.

During the past forty years a very large amount of research has been carried out in connection with the constitution of basic slag, and in 1911 Kroll (1) very aptly summarised the principle facts connected with the subject.

Briefly, the principal phosphates that have been found to exist in a basic slag are as follows: †

Silico-carnotite	$3CaO.P_2O_5: 2CaO.SiO_2$.
Hilgenstockite	$4CaO.P_2O_5$.
Steadite	$3(3CaO.P_2O_5): 2CaO: 2CaO.SiO_2$.
Thomasite	$6CaO.P_2O_5: 2FeO.SiO_2$.

There does not appear to be any reference to crystals taken from a basic slag containing fluoride, although Hilgenstock certainly made use of calcium fluoride in order to lower the melting point of his fusions in his attempt to produce tetrabasic phosphate of lime in the laboratory, despite the fact that the addition of fluorspar to a basic slag was known to cause a very marked reduction in the citric acid solubility value.(6)

Owing to the variable nature of the comparison of basic slag the author felt that the only satisfactory way to determine the effect of calcium fluoride was to prepare synthetically the compounds which are presumed to exist in a basic slag. To do this successfully it was necessary to have a suitable method for the determination of uncombined lime in the fusions, and after considerable delay a method was decided upon which appeared to fulfil all the necessary conditions. A second difficulty also arose with regard to the production of pure fused products, but this was also overcome.

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* Report received April 8, 1920.

† The formulæ and nomenclature of the compounds are those adopted by Kroll, and not necessarily those assigned by the original investigators.

Experimental Work.

Preparation of the Synthetic Phosphates.

The author realised that in order to ensure complete combination a very high temperature would be required to prepare the fusions, and as it was essential that these should be free from all extraneous matter it was clearly impossible to employ a crucible of the refractory type (such as magnesia, &c.), and even platinum could not be considered because of the high temperatures to which the fusions would be subjected. Several methods were tried, including that described by Blome,(7) wherein the operation is performed by fusing a cone of the mixture on a bed of the same material with an oxy-coal-gas flame. This method was, however, discarded, owing to incompleteness of fusion, in favour of the following.

The necessary quantities of materials to be fused were intimately mixed in a shaking machine for half an hour and the mixture moistened with a very weak solution of starch (about 1 cubic centimetre of solution per gramme of mixture), after which it was moulded into sticks by forcing through a glass tube ⅜ inch in diameter, and then dried in a water-oven. The dried stick was suspended by means of a platinum wire and the lower end heated by an oxy-coal-gas blow-pipe, the fused material being allowed to drip into a platinum dish below. The product in all cases was of the nature of a glass, as it was impossible to obtain crystals by this method.

Compositions of Materials Used.

	Per Cent.
Calcined tribasic phosphate of lime (Griffin).	
Phosphoric acid	45·75
Silica	nil
Lime	54·25
Calcined tribasic phosphate of lime prepared according to Ramsay.(18)	
Phosphoric acid	45·80
Silica	nil
Lime	54·20

Calcium Fluoride. (Acid washed and calcined.)

	Per Cent.
Calcium fluoride	99·68
Solubility in 2 per cent. citric acid solution	nil
Precipitated silica :	
Silica	99·90
Starch :	
Ash	0·14

Starch solution contains 2 grammes of starch in 250 cubic centimetres of distilled water.

Pure lime precipitated as carbonate washed and calcined.

Calcium oxide . . . . 100·00 per cent.

Solvents.

*Ammonium Citrate Reagent.**—100 grammes citric acid crystals dissolved in water, neutralised with ammonia and 10 grammes free citric acid added. The whole made up to one litre, cooled and used at a temperature of 16° C.

Citric Acid Reagent.—2 per cent. solution used at a temperature of 16° C.

Estimation of the Uncombined Lime.

The method used in the past to estimate uncombined lime in fused masses was to treat the mass with sugar solution to dissolve out the uncombined lime present. This method is by no means exact. The investigations by Philippi (8) showed that out of 0·2 grammes of calcium ortho-silicate 38·6 per cent., and out of meta-silicate 7·6 per cent., of lime was dissolved when shaken with 200 cubic centimetres of 10 per cent. grape sugar solution. On this account Blome (9) adopted a method whereby the uncombined lime was estimated with sulphuretted hydrogen. This method consisted in passing pure dry sulphuretted hydrogen over a weighed quantity of the material contained in a porcelain boat, which was placed in a hard glass tube heated to 800°C. At the end of three hours the sulphuretted hydrogen was stopped and dry hydrogen passed over while the tube was being allowed to cool. The gain in weight being due to the sulphide formed.

The author, however, was unable to consider this method on account of the presence of iron oxide in several of the fusions.

Morrison's (10) method was also examined, but was considered to give high results owing to the slight solubility and dissociation of tribasic phosphate of lime in water.

A modification of Blome's method was finally drawn up and used throughout the research.

* Stead, Cleveland Institution of Engineers, 1895.

This method consisted in passing steam over a weighed quantity of the material contained in a platinum boat which in turn was placed in a silica tube surrounded by a hot-air jacket, the temperature of which was maintained at 140° C. Fig. 14 illustrates the apparatus used.

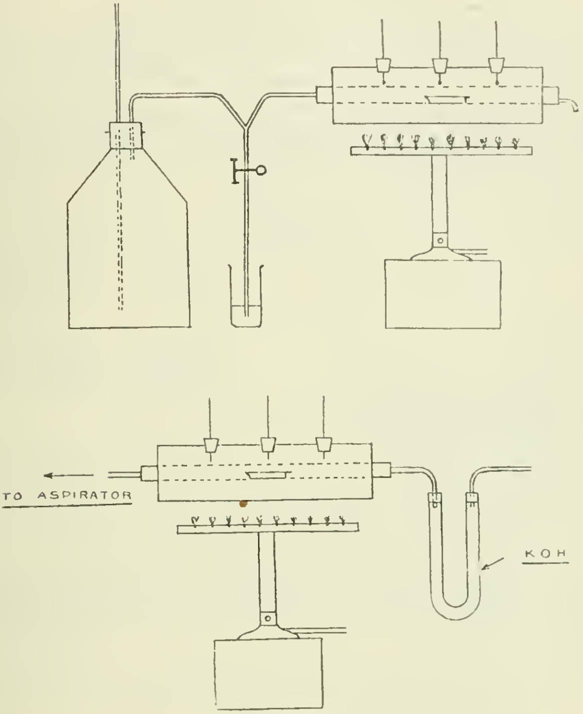

Fig. 14.

Procedure.—Having brought the hot-air jacket to the required temperature, a quantity of the material to be tested was weighed into a previously heated and weighed platinum boat; this in turn was placed in the centre of the silica tube and steam passed over for a period of four to seven hours, at the end of which time the steam generator and Y tube were disconnected and a tube containing solid caustic potash substituted; the open end of the silica tube at the same time being connected with a large aspirator.

after which a slow stream of dry air was drawn through the apparatus, the temperature of 140° C. still being maintained. After drying for the necessary period the platinum boat was withdrawn, allowed to cool in a desiccator containing caustic potash and calcium chloride, and again weighed. The gain in weight was equal to the water taken up by the uncombined lime on hydration, 1 gramme of lime on hydration gaining 0·321 grammes of water, the hydration being confirmed by subsequent calcination. The following experiments were carried out in order to establish the accuracy of the method:

TABLE I.

Experiment.	Materials and Quantity.	Gain in Weight.	Equivalent Free Lime.	Theoretical Free Lime.
		Grammes.	Grammes.	Grammes.
a	0·1 gramme pure burnt lime	0·0320	0·100	0·100
b	2·0 grammes $3CaO.P_2O_5$	0·0020	0·0062	...
c	1·0 gramme $3CaO.P_2O_5$ mixed with 0·1 gramme CaO	0·0335	0·1042	0·1030
d	0·2 gramme CaF_2	nil	nil	nil
e	1·0 gramme of a fusion of a mixture of CaF_2 and CaO	0·0785	0·244	0·240 *

It was considered that the above results were sufficiently accurate to warrant the use of this method throughout the research.

PRELIMINARY EXPERIMENTS.

Series I.

Being a series of experiments showing variation in solubility values when ammonium citrate and citric acid are used as solvents.

(*a*) 2·5 grammes calcined tribasic phosphate of lime (Griffin) treated with 500 cubic centimetres 2 per cent. citric acid solution and rotated for thirty minutes at forty revolutions per minute.

	Per Cent.
Total phosphoric acid	45·75
Soluble phosphoric acid	25·35
Parts soluble per 100 of P_2O_5	55·41

---

* Determined by analysis and calculation.

(*b*) Two grammes calcined tribasic phosphate of lime (Griffin) treated with 200 cubic centimetres of ammonium citrate solution, rotated for thirty minutes at forty revolutions per minute and allowed to stand twenty hours before filtering.

	Per Cent.
Soluble phosphoric acid	4·97
Parts soluble per 100 of P_2O_5	10·86

This experiment showed a slightly higher result than that recorded by Stead (Cleveland Institution, 1895).

(*c*) A third experiment was made with the same quantities as in (*b*), dispensing with the rotating machine and shaking by hand at intervals during twenty hours. The following results were obtained :

	Per Cent.
Soluble phosphoric acid	3·57
Parts soluble per 100 of P_2O_5	7·80

This result agreed very closely with Stead's figure of eight parts soluble per 100 of P_2O_5.

From experiments (*a*), (*b*), and (*c*) it is clear that the citric acid solution gives considerably higher results, confirming experiments conducted by Messrs. Gerlach and Passon,(19) who state that when testing slags in three instances they obtained higher results by the 2 per cent. citric acid solution. O. Foerster,(20) in criticising Messrs. Gerlach and Passon's results, also confirms the increased solvent power of 2 per cent. citric acid over ammonium citrate solution.

In view of the above it was decided to abandon the ammonium citrate and use only 2 per cent. citric acid solution throughout the following experiments.

Series II.

Experiments were conducted with a view to establishing the maximum solubility of tribasic phosphate of lime in 2 per cent. citric acid solution with special regard to the fineness. The tribasic phosphate of lime was fused by the method already described, the total phosphoric acid estimated, and the following tabulated experiments carried out :

TABLE II.—*Solubility of Fused Tribasic Phosphate of Lime* (*Griffin*) *in* 500 *cubic centimetres of* 2 *per cent. Citric Acid Solution, shaken in the Rotating Machine for thirty minutes at forty revolutions per minute.*

Experiment.	Quantity Treated.	Condition of Fused Material.	Total P_2O_5.	Soluble P_2O_5.	Soluble P_2O_5 per 100 of P_2O_5.
	Grammes.		Per Cent.	Per Cent.	Per Cent.
a	5·0	Passed through 100-mesh sieve	45·70	33·29	72·84
b	2·5	,,	45·70	40·73	89·12
c	1·0	,,	45·70	43·90	96·06
d	2·5	Ground to a flour	45·70	42·30	92·55
e	1·0	,,	45·70	45·40	99·34

In view of Mr. Ramsay's discussion on the composition of commercial tribasic phosphate of lime, and in order to obtain comparisons with the material used in the above experiments, a quantity of tribasic phosphate of lime was prepared according to his method, fused, the total phosphoric acid estimated, and the solubility experiments shown in Table IIA. carried out.

TABLE IIA.—*Solubility of Fused Tribasic Phosphate of Lime* (*Ramsay*) *in* 500 *cubic centimetres of* 2 *per cent Citric Acid Solution, shaken in the Rotating Machine for thirty minutes at forty revolutions per minute.*

Experiment.	Quantity Treated.	Condition of Fused Material.	Total P_2O_5.	Soluble P_2O_5.	Soluble P_2O_5 per 100 of P_2O_5.
	Grammes.		Per Cent.	Per Cent.	Per Cent.
f	5·0	Passed through 100-mesh sieve	45·80	37·61	82·12
g	1·0	Ground to a flour	45·80	44·59	97·36

It would appear that there is some difference in the phosphates, but the author considers this to be more a question of mechanical condition rather than difference in composition.

After consideration of the results given in Tables II. and IIA. the author decided to use Griffin's tribasic phosphate of lime throughout the fusions, and that 1 gramme solubility tests should be adopted throughout the greater part of the subsequent experiments.

Series III.

The Effect of Calcium Fluoride on Synthetic Phosphates.

Fusions consisting of Mixtures of Tribasic Phosphate of Lime and Calcium Fluoride.—Five melts were made containing varying quantities of calcium fluoride and tribasic phosphate of lime which were subsequently ground and refused three times to ensure complete combination; the analysis is shown in Table III., all constituents being determined with the exception of the fluoride which, owing to difficulty and inaccuracy of the known methods for the determination of fluorine in the presence of phosphates, it was found better to calculate indirectly according to the equation:

$$22:78::\overset{\text{Per Cent.}}{100}-(P_2O_5+CaO+CaF_2\text{ expressed as }\overset{\text{Per Cent.}}{CaO}):x\,CaF_2.$$

The solubility tests were carried out on 1 gramme portions ground to a flour and treated with 500 cubic centimetres of 2 per cent. citric acid solution as in experiment (*c*), Table II.

TABLE III.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Total CaO per cent. . .	54·30	55·07	56·25	60·00	61·50	62·65
Total P_2O_5 ,, . .	45·70	44·60	43·19	38·09	36·31	30·13
Estimated free CaO per cent. .	0·31	1·25	3·55	10·30	13·15	9·06
Calculated analysis per cent.:						
$3CaO.P_2O_5$ . . .	99·78	97·37	94·30	83·17	79·28	65·78
Free CaO . . .	0·22	1·46	3·72	10·06	12·95	8·62
CaF_2	nil	1·17	1·98	6·77	7·77	25·60
Solubilities per cent.:						
Soluble P_2O_5 . . .	45·40	36–15	30·97	15·13	13·85	8·36
Soluble CaO . . .	...	44·25	40·50	28·05	29·25	18·50
Parts P_2O_5 soluble per 100 of P_2O_5 . . .	99·34	81·05	71·70	39·72	38·14	27·74
Parts P_2O_5 soluble per 100 of $3CaO.P_2O_5$ . .	45·49	37·12	32·84	18·19	17·47	12·71
Parts CaF_2 present per 100 of $3CaO.P_2O_5$ . .	nil	1·20	2·10	8·14	9·80	37·92

The parts of P_2O_5 soluble per 100 of $3CaO.P_2O_5$ have been plotted in Fig. 15, which shows very distinctly the rapid fall in solubility down to a point corresponding roughly to eight parts calcium fluoride added to 100 parts tribasic phosphate of lime.

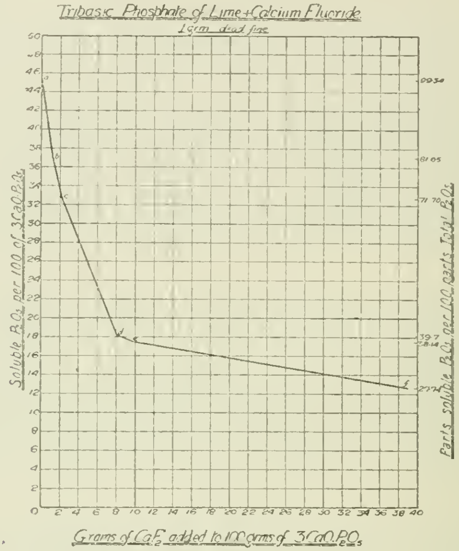

FIG. 15.

It is also noticeable that the calcium fluoride has decomposed to a considerable extent during fusion, and the calcium oxide formed does not appear to have combined to form tetrabasic phosphate at the temperature attained during fusion, also the lime so formed is completely soluble in citric acid solution.

Preparation for Tetrabasic Phosphate of Lime.

The preparation of this compound has been attempted by at least three investigators, Hilgenstock,$^{(11)}$ Stead,$^{(12)}$ and Blome,$^{(13)}$ and only in the case of the last-named was an estimation of the free lime made. The purest compound obtained by Blome contained 6 05 free lime, thus leaving 33 5 per cent. of uncombined tribasic phosphate of lime in the melt.

Hilgenstock's attempt may be disregarded owing to his use of calcium fluoride in order to reduce the fusion temperature; although the interesting fact may be recorded that crystals in the shape of hexagonal needles were obtained.

The author of the present memoir prepared a mixture of tribasic phosphate of lime and pure lime in the required proportions and subjected it to fusion by means of the oxy-coal-gas blow-pipe. The mass melted fairly readily and gave the following analysis:

	Per Cent.
Total phosphoric acid	37·97
Total lime	62·03
Estimated free lime	3·80

This meant that 2·14 per cent. free lime required an addition of tribasic phosphate of lime to form tetrabasic phosphate of lime, and 1·66 per cent. of lime was also uncombined, although the necessary amount of tribasic phosphate was present. The probable composition was therefore:

	Per Cent.
Tetrabasic phosphate of lime	87·01
Tribasic phosphate of lime	9·19
Uncombined lime	1·66
Free lime in excess	2·14

The melt obtained from this first fusion was mixed with the necessary amount of tribasic phosphate and refusion attempted. It was found, however, that this could only be accomplished with greatest difficulty owing to the infusibility of the compound. An analysis of the melt gave the following results:

	Per Cent.
Total phosphoric acid	38·79
Total lime	61·21
Estimated free lime	1·70

This meant a probable composition of:

	Per Cent.
Tetrabasic phosphate	89·00
Tribasic phosphate	9·30
Uncombined lime	1·68
Free lime excess	0·02

Solubility tests gave the following results:

	5 Grammes 100-Mesh. Per Cent.	1 Gramme ground to Flour. Per Cent.
Soluble phosphoric acid	22·78	30·73
Soluble lime	38·10	Not estimated
Parts P_2O_5 soluble per 100 parts P_2O_5	58·73	79·22

As there was still a large proportion of tribasic phosphate in the melt it was again subjected to fusion. This was found to be impossible with oxy-coal-gas and the oxy-acetylene blow-pipe was used. The analysis of the final melt was:

	Per Cent.
Total phosphoric acid	38·79
Total lime	61·21
Estimated free lime	0·90

Probable composition:

	Per Cent.
Tetrabasic phosphate	94·12
Tribasic phosphate	4·98
Uncombined lime	0·90

Solubility tests on the material showed:

	5 Grammes 100-Mesh. Per Cent.	1 Gramme ground to Flour. Per Cent.
Soluble phosphoric acid	8·34	28·03
Soluble lime	14·15	Not estimated
Parts P_2O_5 soluble per 100 parts P_2O_5	21·50	72·26

The remarkably low solubility of this material is in agreement with Dr. Stead's investigation on the square plates which he obtained from slowly cooled basic slag, and the above uncombined lime results appear to explain the reason for the high solubility of his synthetic tetrabasic phosphate.

Series IV.

Fusions consisting of Mixtures of Tetrabasic Phosphate of Lime and Calcium Fluoride.—The previously prepared tetrabasic phosphate of lime being considered of sufficient purity three melts were made containing varying amounts of tetrabasic phosphate and calcium fluoride, the fluorine percentage being determined as in Series III. Solubility tests were carried out on 1 gramme portions as before. The results are recorded in Table IV.

The solubility results expressed per 100 of $3CaO.P_2O_5$ are shown in Fig. 16. The point on the dotted line represents solubility of sample *b*, as shown in Table IV. It would appear from an examination of this table that all the calcium fluoride present has not been combined, probably due to the fact that samples *c* and *d* were prepared first and were fused three times, whereas sample *b*, prepared later, was only fused once, owing to the blow-pipe nozzle being destroyed.

TABLE IV.

	a.	*b.*	*c.*	*d.*
Total CaO per cent.	61·21	62·10	62·60	68·30
Total P_2O_5 ,, . . .	38·79	35·80	33·70	16·24
Estimated free CaO per cent. .	0·90	8·70	13·75	9·06
Calculated analysis per cent. :				
Calcium fluoride	nil	7·45	13·12	54·81
Solubilities per cent. :				
Soluble P_2O_5	28·03	12·90	10·03	9·24
Soluble CaO	not estimated	29·25	31·00	25·00
Parts P_2O_5 soluble per 100 parts P_2O_5	72·26	36·03	29·77	56·89
Parts P_2O_5 soluble per 100 parts $3CaO.P_2O_5$	33·09	16·50	13·65	26·05
Parts CaF_2 present per 100 of $3CaO.P_2O_5$	nil	9·53	17·83	154·57

In Table IV., if the calcium fluoride content be calculated to its calcium oxide equivalent the following figures are obtained :

	a.	*b.*	*c.*	*d.*
CaF_2 as CaO	nil	5·35	9·42	39·35

Adding to these the estimated free lime and deducting the result from the total lime, the lime in combination with the phosphoric acid is obtained thus :

	a.	*b.*	*c.*	*d.*
CaF_2 as CaO	nil	5·35	9·42	39·35
Estimated free lime	0·90	8·70	13·75	9·06
On adding	0·90	14·05	23·17	48·41
Total lime	61·21	62·10	62·60	68·30
Less	0·90	14·05	23·17	48·41
CaO combined with P_2O_5 . .	60·31	48·05	39·43	19·89

It is clear that in samples *c* and *d* there is only sufficient lime to form tribasic phosphate with the total phosphoric acid present. In the case of sample *a* it exists as tetrabasic phosphate, and in sample *b* there is some quantity of tetrabasic phosphate still undecomposed, as shown below :

	b.	*c.*	*d.*
Total P_2O_5	35·80	33·70	16·24
CaO required to form $3CaO.P_2O_5$ (theoretical)	42·37	39·88	19·22
Actual CaO available for combination with P_2O_5	48·05	39·43	19·89

Taking Fig. 15 into consideration and presuming certain data following later in the memoir the author has calculated the probable compositions of the samples *b*, *c*, and *d* on the assumption that an apatite compound of the formula $3(3CaO.P_2O_5).CaF_2$ is formed. The results are given in Table IVA.

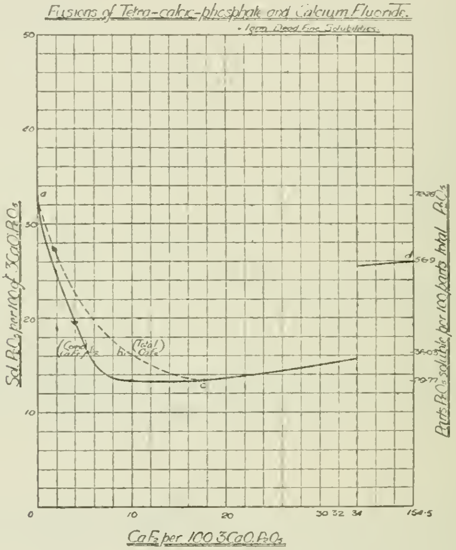

FIG. 16.

TABLE IVA.

	b. Per Cent.	*c.* Per Cent.	*d.* Per Cent.
Tetrabasic phosphate of lime, $4CaO.P_2O_5$.	35·42	nil	nil
Apatite, $3(3CaO.P_2O_5).CaF_2$ . . .	52·20	79·74	38·43
Uncombined calcium fluoride . . .	3·41	6·96	51·84
Uncombined lime	8·70	13·30	9·73

In the case of sample *b*, as explained above, all the tetrabasic phosphate has not been decomposed, and only 4·04 of the calcium fluoride has entered into combination to form apatite. When this combined calcium fluoride is calculated per 100 parts of tribasic phosphate we obtain the figure 5·17 parts CaF_2, and on adjusting the solubility of sample *b* to this quantity of calcium fluoride (point b_2) we obtain a curve in Fig. 16 corresponding very closely to that in Fig. 15.

Preparation of Silico-Carnotite $3CaO.P_2O_5 : 2CaO.SiO_2$.—In order to prepare this compound it was found necessary first to prepare dicalcic silicate, $2CaO.SiO_2$. The necessary quantities of lime and silica were mixed and fused in the oxy-coal-gas flame. These materials appeared to combine fairly readily, a thin clear fusion being produced which fell to powder immediately on cooling, confirming the work of Boudouard (14). The analysis of the melt showed :

	Per Cent.
Silica	34·80
Lime	65·20
Free lime	3·10

showing that 1·66 of the silica was uncombined. A citric acid solubility test on 1 gramme gave :

	Per Cent.
Soluble lime	65·15
Soluble silica	32·90

Insoluble portion was burnt off and weighed and amounted to 1·70 per cent. silica, thus confirming the free lime test. The material was considered pure enough to proceed without further fusion.

A mixture of dicalcic silicate and tribasic phosphate of lime was made in the proportions necessary to form silico-carnotite $3CaO.P_2O_5 : 2CaO.SiO_2$ and fused in the oxy-coal-gas blowpipe. The melt gave the following analysis :

	Per Cent.
Silica	12·35
Phosphoric acid	28·73
Total lime	58·92
Estimated free lime	1·62
Calculated free lime	1·87

showing that the small quantity of uncombined silica in the dicalcic silicate has apparently displaced a little of the phosphoric acid which in the course of fusion was volatilised. Solubility tests gave the following results:

	5 Grammes 100-Mesh. Per Cent.	1 Gramme ground to Flour. Per Cent.
Soluble P_2O_5	28·54	28·73
Soluble SiO_2	12·00	12·35
Soluble CaO	58·20	58·92
Parts P_2O_5 soluble per 100 of P_2O_5 .	99·34	100·00

The 1 gramme portion was completely dissolved within two minutes of the commencement of the shaking, thus confirming the extreme solubility of silicophosphates as stated by Stead.

Series V.

Fusions consisting of Mixtures of Silico-Carnotite and Calcium Fluoride.—Four fusions were made, consisting of varying quantities of silico-carnotite and calcium fluoride, and the melts analysed. See Table V.

TABLE V.

Sample.	*a.*	*b.*	*c.*	*d.*	*c.*
Total SiO_2 per cent. . . .	12·35	12·30	11·95	9·90	7·55
,, P_2O_5 ,, . . .	28·73	28·54	27·78	25·82	23·17
,, CaO ,, . . .	58·92	59·00	59·35	62·35	65·00
Estimated free CaO per cent. .	1·62	1·55	1·55	8·06	12·13
Calculated analysis:					
$2CaO.SiO_2$ per cent. . . .	35·40	35·26	34·26	28·38	21·65
$3CaO.P_2O_5$	62·73	55·51	21·79	nil	nil
$3(3CaO.P_2O_5).CaF_2$ per cent. .	nil	7·36	42·12	61·10	54·82
Free CaO per cent. . . .	1·87	1·87	1·83	8·41	12·60
Free CaF_2 ,, . . .	nil	nil	nil	2·11	10·93
Total CaF_2 per cent. . . .	nil	0·57	3·26	6·84	15·17
Parts CaF_2 per 100 of $3CaO.P_2O_5$ when all P_2O_5 is calculated to $3CaO.P_2O_5$	nil	0·91	5·37	12·13	30·00

TABLE VA.—*Solubility Tests. One gramme portions ground to a flour and tested as in previous experiments.*

Sample.	*a.*	*b.*	*c.*	*d.*	*e.*
Soluble SiO_2 per cent	12·35	12·30	11·95	9·90	7·55
Soluble P_2O_5 ,, ...	28·73	24·92	11·53	7·61	7·08
Soluble CaO ,, ...	58·92	54·70	38·00	37·10	36·30
Parts P_2O_5 soluble per 100 of P_2O_5 .	100·00	87·32	41·50	29·47	30·56
Parts P_2O_5 soluble per 100 of $3CaO.P_2O_5$	45·80	39·99	19·01	13·50	13·99

These solubilities have been plotted in Fig. 17.

It was not thought necessary in view of the three curves obtained to continue with the preparation of the fourth phosphate,

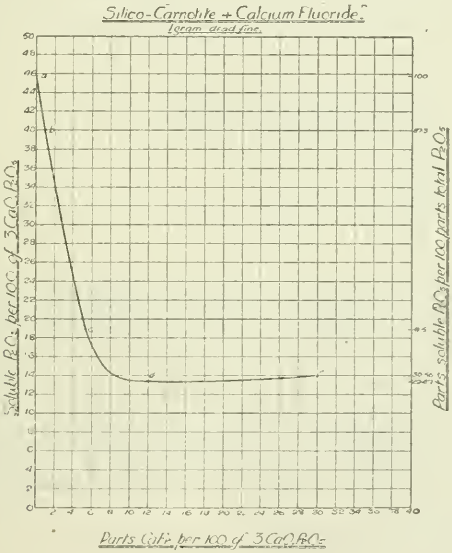

FIG. 17.

Steadite, and owing to the difficulty of obtaining a non-oxidising atmosphere the author was unable to prepare the fifth phosphate, Thomasite.

Preparations were therefore made to produce fusions of a citric-soluble basic slag mixed with varying proportions of calcium fluoride.

Series VI.

Fusion of Basic Slag with Calcium Fluoride.—The slag selected for this purpose had the following analysis:

	Per Cent.
Silica	11·20
Ferrous oxide	14·79
Ferric oxide	7·00
Alumina	7·89
Phosphoric acid	14·48
Manganous oxide	0·37
Calcium oxide	39·10
Magnesium oxide	5·07
Total iron	16·40
Uncombined lime	nil
Soluble P_2O_5 (1 gramme test)	12·58
Parts P_2O_5 soluble per 100 parts P_2O_5	86·88
Parts P_2O_5 soluble per 100 parts of $3CaO.P_2O_5$	39·79

With this material and calcium fluoride the following mixtures were made:

a. Original slag re-fused without addition of CaF_2.
b. 100 parts slag + 2 parts CaF_2.
c. 100 ,, ,, 4 ,, ,,
d. 100 ,, ,, 6 ,, ,,
e. 100 ,, ,, 8 ,, ,,
f. 100 ,, ,, 10 ,, ,,
g. 100 ,, ,, 15 ,, ,,
h. 100 ,, ,, 20 ,, ,,

The analyses of these samples after fusion are given in Table VI. The calcium fluoride content was obtained by calculation from the dilution of the total iron content due to CaF_2, lime (from decomposition of part of the CaF_2), and oxygen due to the oxidation of part of the ferrous oxide during fusion. By calculating the percentage analysis back to the original iron content of the slag, the total dilution is obtained. The calculation is as follows:

If A = Total dilution.
B = Dilution due to oxidation of FeO.
C = Calcium fluoride added.
x = Dilution due to CaF_2 actually present.

Then $$A-B=\text{dilution due to } CaF_2+CaO,$$
and $$A-B-x=\text{dilution due to } CaO.$$

Then $$x+(A-B-x)\frac{78}{56}=C.$$

Solving: $$x=\frac{78A-78B-56C}{22}$$

The author realised that the accuracy of the results obtained by this calculation depends in turn upon the accuracy of the iron estimation. There has therefore been added at the bottom of Table VI. the calcium fluoride which would be present if

TABLE VI.

Sample.	a.	b.	c.	d.	e.	f.	g.	h.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Ferrous oxide (by analysis)	0·77	3·86	3·47	2·31	2·44	4·37	5·40	4·50
Ferric oxide	22·21	18·50	18·57	19·50	19·07	16·64	14·79	14·86
Total iron (by analysis)	16·15	15·95	15·70	15·45	15·25	15·05	14·55	13·90
Calcium fluoride	nil	0·63	1·18	1·58	1·48	2·21	3·05	7·69
Lime from calcium fluoride decomposed	nil	0·94	1·90	2·92	4·28	5·00	7·37	6·64
Phosphoric acid * (calculated)	14·26	14·08	13·86	13·64	13·46	13·29	12·82	12·27
Free lime (by analysis)	nil	nil	nil	nil	nil	nil	nil	nil
Parts CaF_2 present per 100 parts $3CaO.P_2O_5$	nil	2·06	3·93	5·31	5·03	7·65	10·90	28·80
CaF_2 present if 0·05 per cent. Fe is deducted	...	1·74	2·29	2·70	2·62	3·38	4·29	8·98
CaF_2 present if 0·05 per cent. Fe is added	...	nil	0·07	0·41	0·32	1·01	1·86	6·45

TABLE VIA.—*Solubility Tests carried out on* 1 *gramme Portions ground to a Flour.*

Sample.	a.	b.	c.	d.	e.	f.	g.	h.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total P_2O_5	14·26	14·04	13·93	13·70	13·46	13·22	12·80	12·20
Soluble P_2O_5	13·61	11·94	9·63	8·92	8·68	8·12	7·62	5·97
Parts P_2O_5 soluble per 100 parts P_2O_5	95·44	85·04	69·13	65·11	64·48	61·42	59·53	48·93
Parts P_2O_5 soluble per 100 parts $3CaO.P_2O_5$	43·71	38·95	31·66	29·82	29·53	28·13	27·26	22·41

---

* The P_2O_5 by analysis is given in Table VIA.

an allowance of an error of ± 0·05 per cent. iron be made. This does not effect the solubility determination except as regards the location of the respective points on the solubility curve shown in Fig. 18.

These solubilities have been plotted on the curves shown in Figs. 18 and 19. The shaded portions representing the solubilities when the fluoride content lies within this area, based on the plus or minus extremes shown in Table VI.

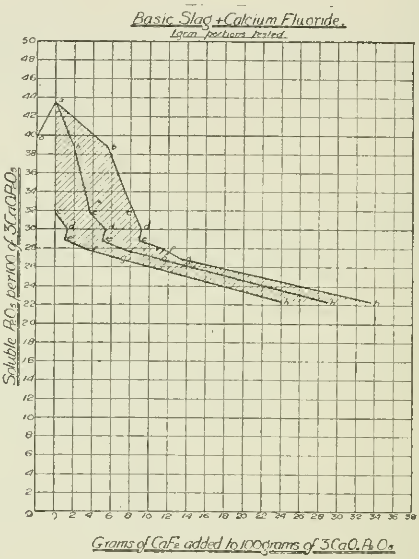

FIG. 18.

In addition to these the solubility of 5-gramme portions of the slags passed through a 100-mesh sieve have been estimated and the corresponding curves plotted in Figs. 19 and 20. The figures are given in Table VIB.

On examining the results of Series VI. it will be noticed that the solubility of the original slag is very much increased by remelting. The only alteration in the chemical analysis being the oxidation of the ferrous oxide to the ferric state. The solubility curves do not follow exactly the course of the tribasic phosphate curve, but this is obviously due to the phosphoric

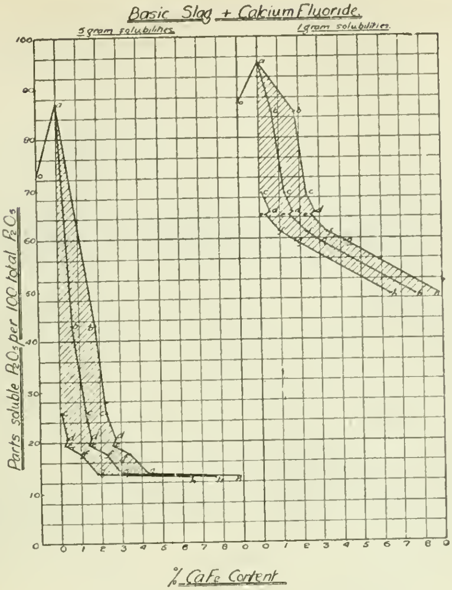
Basic Slag + Calcium Fluoride.
5 gram solubilities
1 gram solubilities
Parts soluble P2O5 per 100 total P2O5
0
10
20
30
40
50
60
70
80
90
100
0 1 2 3 4 5 6 7 8
0 1 2 3 4 5 6 7 8 9
a
b
c
d
e
f
g
h
% CaF2 Content

FIG. 19.

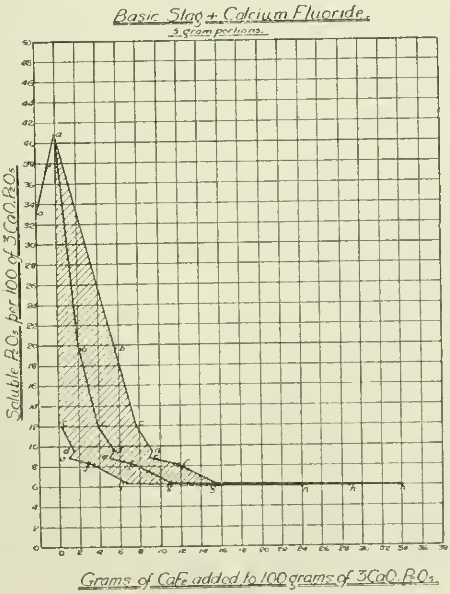
Basic Slag + Calcium Fluoride.
5 gram portions.
Soluble P2O5 per 100 of 3CaO.P2O5
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38
a
b
c
d
e
f
g
h
Grams of CaF2 added to 100 grams of 3CaO.P2O5

FIG. 20.

acid content in the quantities of material taken, and is confirmed by the comparison of Figs. 18 and 20, but the outstanding feature remains the same, namely, that the solubility of the phosphate falls rapidly until the ratio $CaF_2/3CaO.P_2O_5$ is approximately 8/100.

TABLE VIb.

Sample.	a.	b.	c.	d.	e.	f.	g.	h.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total P_2O_5 .	14·26	14·04	13·93	13·70	13·46	13·22	12·80	12·20
Soluble P_2O_5 .	12·74	6·05	3·64	2·86	2·65	2·41	1·79	1·60
Parts P_2O_5 soluble per 100 parts P_2O_5 . .	89·34	43·09	26·13	20·88	19·69	18·23	13·98	13·11
Parts P_2O_5 soluble per 100 parts $3CaO.P_2O_5$.	40·91	19·73	11·97	9·56	9·05	8·35	6·40	6·00

Deductions (Series I. to VI.).

No matter what form of compound the phosphoric acid assumes in a basic open-hearth slag the addition of calcium fluoride to the molten mass appears to bring about the formation of a compound consisting of approximately 8 parts of calcium fluoride united with 100 parts of tribasic phosphate of lime, which agrees closely with the formula for apatite, $3(3CaO.P_2O_5).CaF_2$, wherein 100 parts 3CaO P O_5 unite with 8·37 parts CaF_2.

On the addition of calcium fluoride to a fusion of tetrabasic phosphate free lime is liberated, and in the case of silicophosphate dicalcic silicate is liberated.

If these conclusions be correct one would expect to obtain crystals of apatite from a basic slag made with large additions of fluorspar and allowed to cool slowly. With the permission of the Skinningrove Iron Co., Ltd., this experiment was carried out.

Crystals from a Slowly-cooled Basic Slag made with the Addition of Fluorspar.—On breaking open the cooled slag-ball the centre was found to be filled with a mass of needle crystals about $\frac{1}{64}$ inch to $\frac{1}{32}$ inch in diameter, and from $\frac{1}{8}$ inch to $\frac{5}{16}$ inch in length. Surrounding this mass was a denser area containing needle crystals in a matrix. Mr. Hallimond (Geological Survey) kindly undertook the microscopic investigation of the denser material and also of the isolated crystals, and a photomicrograph of the denser material is given in Fig. 22. The following is the description given by Mr. Hallimond :

" *Apatite Slag.*—The chief constituent is apatite in parallel or interlacing hexagonal prisms terminated by the base. Among these occur dendrites of a deep brown substance (spinel ?) which are sometimes partially included in the apatite. The separation of this constituent has apparently continued throughout the freezing of the slag ; it forms in places a well-defined peg structure in the outer layers of the apatite prisms, normal to the axis, and also forms a large part of the ground-mass of the slag, in which it is found in irregular intergrowth with colourless ophitic crystals of a silicate that has fairly marked birefringence, and it is possibly a monticellite. The apatite forms about 60 per cent. of the sample."

The isolated crystals are described as apatite in hexagonal prisms.

Mr. L. J. Spencer (Natural History Section, British Museum) has also examined the crystals, and describes them as artificial apatite. No terminal faces were found, but some accurate determinations of the refractive indices were made through clear prisms.

On breaking up the detached crystals it was found that a greyish brown material could be separated by an electro-magnet. This material was retained for further investigation.

A considerable quantity of the clean needles was collected and subjected to analysis, the following results being obtained :

	Per Cent.
Silica	1·10
Alumina	nil
Iron expressed as peroxide	0·57
Manganous oxide	0·14
Lime and calcium fluoride expressed as calcium oxide	56·30
Phosphoric acid	37·39
Fluorine *	6·50
Vanadic oxide	nil
Chromic oxide	nil
Magnesium oxide	trace

---

* Fluorine determination in slag presents many difficulties, and the above figure is an average of results by several analytical methods. It is hoped to shortly confirm this figure by an independent analyst.

This analysis may be summated as follows:

	Per Cent.
Apatite	88·47
Excess calcium fluoride	6·50
Dicalcic silicate	3·15
Impurities	1·88

On washing the crushed crystals with cold 2 per cent. solution of hydrochloric acid it was found that the bulk of the dicalcic silicate was removed, leaving the apatite and free calcium fluoride insoluble, together with the iron and manganous oxides.

A citric acid-solubility test on a 5-gramme portion of the unwashed crystals showed 2·04 per cent. soluble phosphoric acid, which is equal to 5·45 parts soluble phosphoric acid per 100 parts of total phosphoric acid, or 2·50 parts soluble phosphoric acid per 100 parts of tribasic phosphate of lime.

One gramme of the crystals ground to a flour and treated with 500 cubic centimetres of 2 per cent. citric acid solution for half an hour at forty revolutions per minute showed 9·82 per cent. soluble phosphoric acid, which is equal to 26·26 parts of soluble phosphoric acid per 100 parts of total phosphoric acid, or 12·03 parts of soluble phosphoric acid per 100 parts of tribasic phosphate of lime.

The result of the 5-gramme test is very similar to that obtained for pure mineral apatite by Robertson (15) and therefore confirms the apatite compound.

The grey magnetic material was ground and concentrated by repeated magnetic separation under benzol with an electromagnet. The analysis after the final cleaning was as follows:

	Per Cent.
Silica	1·30
Alumina	1·84
Ferric oxide	23·29
Ferrous oxide	26·23
Manganous oxide	14·04
Lime	7·40
Magnesia	24·90
Phosphoric acid	1·03

This material was somewhat similar to that described by Dr. Stead in 1887, (16) the principal difference being that Dr. Stead's material contains more lime and less magnesia than the above. There does not appear to be any mineral at all approaching the above in analysis; the simplest explanation would probably be to regard it as a solution of magnetite, ferrous oxide, and manganous oxide in periclase, but at present the only evidence for solution of magnetite in this way is that crystals of magnesia are very deeply stained in bricks from an open-hearth furnace. Until the extent of periclase solid solutions has been ascertained it is impossible to classify the material with certainty.

Summary.

1. When a sufficient quantity of calcium fluoride (fluorspar) is added to a molten basic slag, the whole of the phosphate is converted into apatite, which material has a very low citric acid-solubility value.

2. Owing to the very high temperature required it is extremely probable that pure synthetic tetrabasic phosphate of lime has never before been prepared except in the open-hearth furnace, and then only in the square tabular prisms described by Stead in 1887, and that this material has only a moderate citric acid-solubility value and not the very high one usually associated with this compound.

3. That the hexagonal needle crystals described by Hilgenstock in his attempt to prepare tetrabasic phosphate of lime by adding calcium fluoride were probably apatite crystals.

4. The silicophosphate of lime of the formula

$$3CaO.P_2O_5 : 2CaO.SiO_2$$

is extremely soluble in citric acid solution, and that this or a similar silicophosphate such as Steadite is the form taken by phosphoric acid in extremely soluble basic slags.

5. That free lime does not exist to any extent in the normally produced basic slag (see Appendix), when the P_2O_5 is approximately 14 per cent.

In conclusion, the author wishes to thank the many gentlemen who have assisted with advice and special work, and in particular Mr. R. W. Jackson, who is responsible for the method of preparing the fusions and also for the bulk of the analytical work.

The author realises that the field of investigation of basic slag compounds is extremely wide, and that in this memoir only a very small portion of that field has been covered. Time, however, has precluded any further consideration of the subject.

APPENDIX.

THE EFFECT OF THE ADDITION OF LIME ON THE CITRIC ACID SOLUBILITY OF A BASIC SLAG.

In response to a request from Dr. Stead for some data on the above subject, a series of fusions were made with the slag used in Series VI.

Mixtures in the following proportions were prepared and fused:

a. Original slag as made in open-hearth furnace.
b. Original slag refused.
c. 100 parts of slag + 2 parts of lime.
d. 100 ,, ,, 5 ,, ,,
e. 100 ,, ,, 10 ,, ,,
f. 100 ,, ,, 15 ,, ,,
g. 100 ,, ,, 20 ,, ,,

The resultant melts were ground to pass the 100-mesh sieve, an analysis made, and 5 grammes of each subjected to the citric solubility test.

Sample.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total phosphoric acid	14·48	14·26	14·00	13·80	13·12	12·55	11·99
Total lime . .	39·10	38·50	39·70	41·30	44·00	46·30	48·60
Total silica . .	11·20	11·10	10·90	10·60	10·10	9·60	9·30
Ferrous oxide .	14·79	0·77	1·16	0·26	0·51	nil	0·51
Ferric oxide . .	7·00	22·21	21·29	21·71	20·43	20·00	18·71
Total iron . .	16·40	16·15	15·80	15·40	14·70	14·00	13·50
Total sulphur. .	...	0·068	0·068	0·055	0·041	0·068	0·082
Free lime . .	nil	nil	nil	nil	nil	nil	2·00
Soluble phosphoric acid . . .	10·50	12·74	12·48	11·91	10·82	9·52	8·15
Soluble lime . .	34·55	36·80	35·10	33·80	32·85	30·75	32·80
Soluble silica . .	10·00	10·40	9·80	8·30	9·20	8·70	8·60
Soluble iron . .	0·30	0·60	0·40	2·35	1·40	1·40	2·50
Parts P_2O_5 soluble per 100 parts of P_2O_5 . . .	72·5	89·3	89·1	86·3	82·4	75·9	68·0

From these results it is clear that on remelting the original slag:

1. That the solubility of the phosphate in citric acid solution is considerably increased as explained in Series VI.

2. The addition of lime above that already present in the original slag does not appreciably effect the solubility except as far as the dilution of the phosphate is concerned. Results plotted in Fig. 21.

3. The added lime has apparently combined to form a compound nearly insoluble in citric acid and does not exist in the free state, indicated by the results of the free lime tests and the soluble lime results.

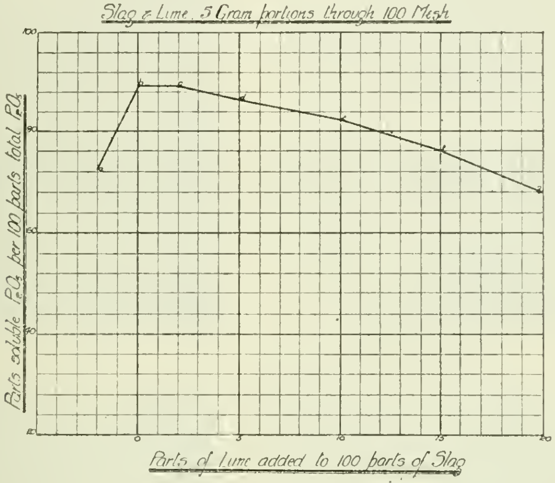

FIG. 21.

4. The silica is almost completely soluble in 2 per cent. citric acid solution.

5. The iron compounds are only slightly soluble in 2 per cent. citric acid solution.

It would appear that the two most important insoluble constituents of the slag were iron oxide and calcium oxide, and on this account a solubility test on 1 gramme of pure lime was carried out. This showed complete solution after half an hour rotation except for a slight milkiness. It must therefore be concluded that the insoluble lime was combined with the iron oxide. In order to investigate the latter point a fusion was made of a mixture of ferric oxide and pure lime; the melt had the following analysis :

	Per Cent.
Ferrous oxide	9·50
Ferric oxide	41·90
Lime	48·60
Free lime (determined)	10·30

A citric-solubility test on 1 gramme gave the following result :

	Per Cent.
Soluble FeO	8·50
Soluble Fe_2O_3	0·92
Soluble CaO	17·00

Deducting the soluble percentage from the total we have :

		Per Cent.
Insoluble material	FeO	1·00
	Fe_2O_3	40·98
	CaO	31·60

Approximating very closely to the compound calcium ferrite (17) $2CaO.Fe_2O_3$, wherein the Fe_2O_3/CaO equals 40·98/28·68.

A portion of the original fused mass was calcined for several hours at a dull red heat and an analysis made :

	Per Cent.
Ferric oxide	52·80
Ferrous oxide	nil
Calcium oxide	47·20
Free lime (determined)	18·90

The interesting increase in the free lime due to calcination points to a combination of ferrous oxide and lime which is decomposed on calcination, although no mineral of this type is known. From these experiments the reason for the insolubility of the lime in the slag and lime series is obvious.

BIBLIOGRAPHY.

(1) *Journal of the Iron and Steel Institute*, 1911, No. II. p. 126.
(2) *Comptes rendus de l'Academie des Sciences de Paris*, 1883, vol. xcvii.
(3) *Stahl und Eisen*, 1887, No. 7, p. 557.
(4) *Journal of the Chemical Society*, 1887, vol. li.
(5) *Stahl und Eisen*, 1908, No. 19, pp. 675–6.
(6) Harbord, "Metallurgy of Steel," p. 189.
(7) *Metallurgie*, 1910, p. 659.
(8) Phillipi, "Dissertation," Charlottenburg, 1908.
(9) Blome, *loc. cit.*
(10) Morrison, *Journal of Agricultural Science*, vol. iii. Part II. p. 161.
(11) See (7).
(12) *Proceedings of the Cleveland Institution of Engineers*, 1895, p. 123.
(13) Blome, *loc. cit.*
(14) Boudouard, *Journal of the Iron and Steel Institute*, 1905, No. I. p. 352.
(15) *Journal of Agricultural Science*, Sept. 1916, vol. viii. Part I. p. 24.
(16) Stead, *Journal of the Iron and Steel Institute*, 1887, No. I. p. 225.
(17) Stead and Ridsdale, *Ibid.*, p. 235.
(18) *Journal of Agricultural Science*, vol. viii. Part III.
(19) *Chemiker-Zeitung*, vol. xx. pp. 87–88.
(20) *Journal of the Iron and Steel Institute*, 1896, No. I. p. 469.

PLATE I.

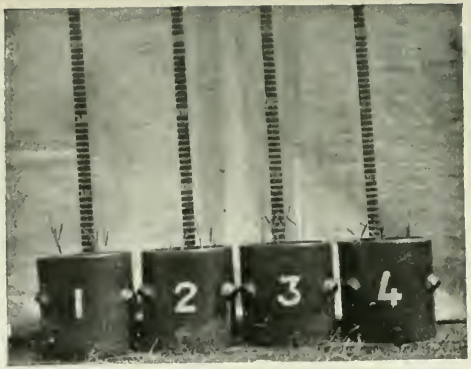

Fig. 3, series I.—Without slag.

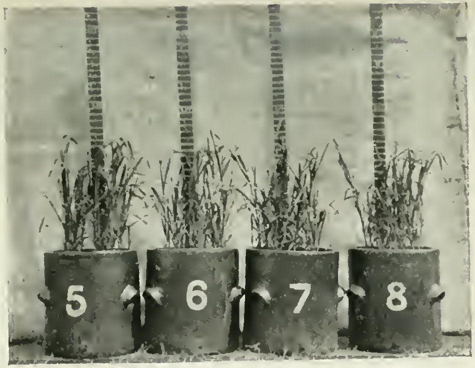

Fig. 4, series II.—Containing Insoluble slag.

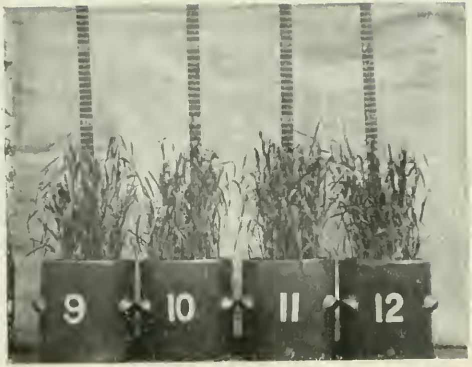

Fig. 5, series III.—Containing Soluble slag.

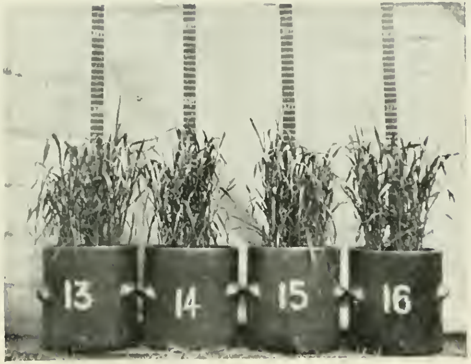

Fig. 6, series IV.—Containing Soluble slag.

Half-grown barley plants.

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PLATE II

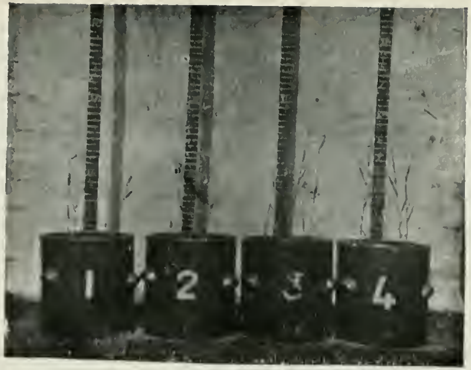

Fig. 7, series I.—Without slag.

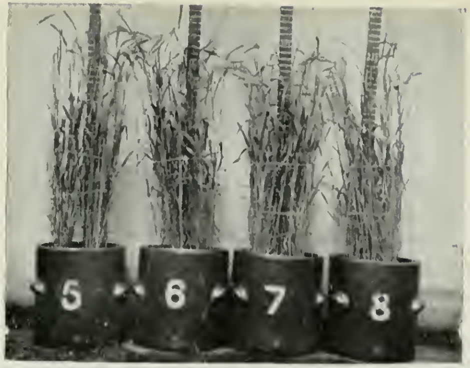

Fig. 8, series II.—Containing Insoluble slag.

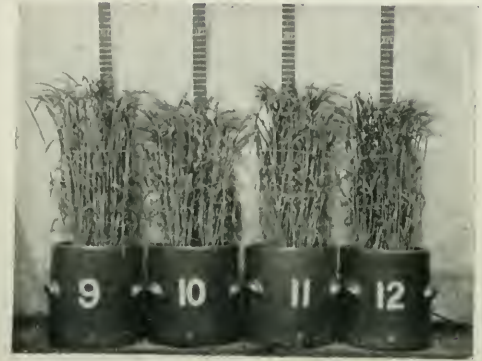

Fig. 9, series III.—Containing Soluble slag.

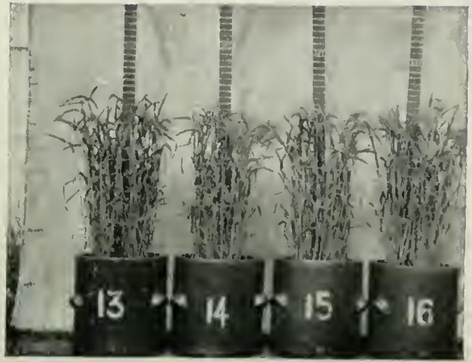

Fig. 10, series IV.—Containing Soluble slag.

Full-grown barley plants.

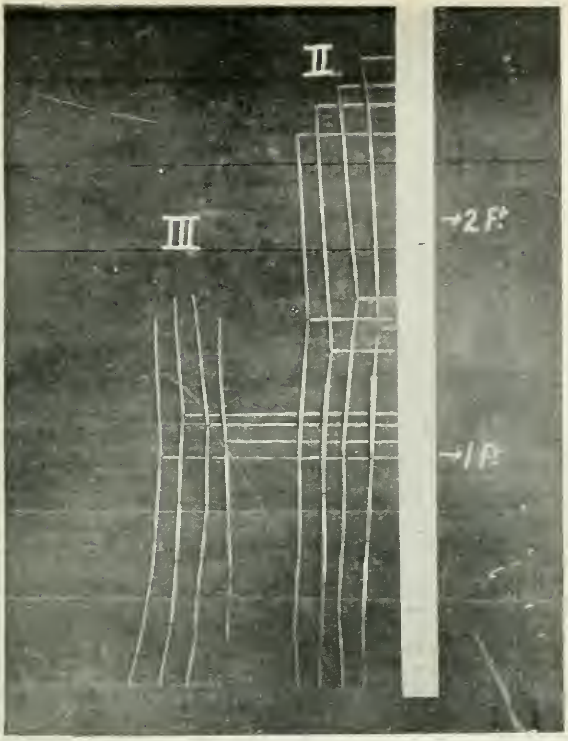
II
III
→2 Ft
→1 Ft

Fig. 11.—Straw from series II and III, showing difference in length of top internode.

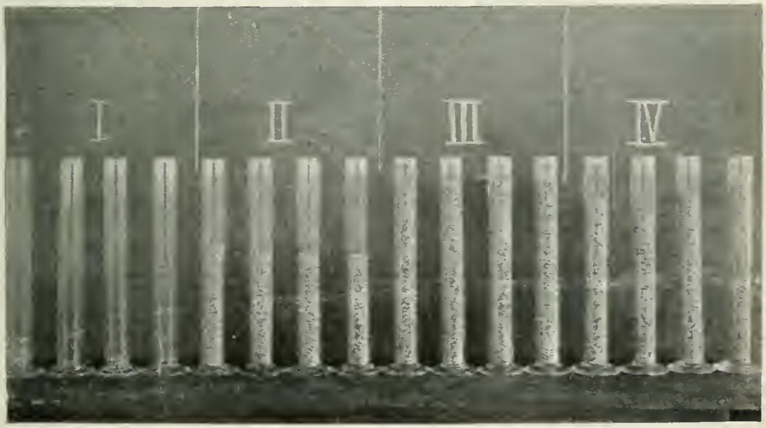

Fig. 13.—Showing difference in bulk of grain in the four series.

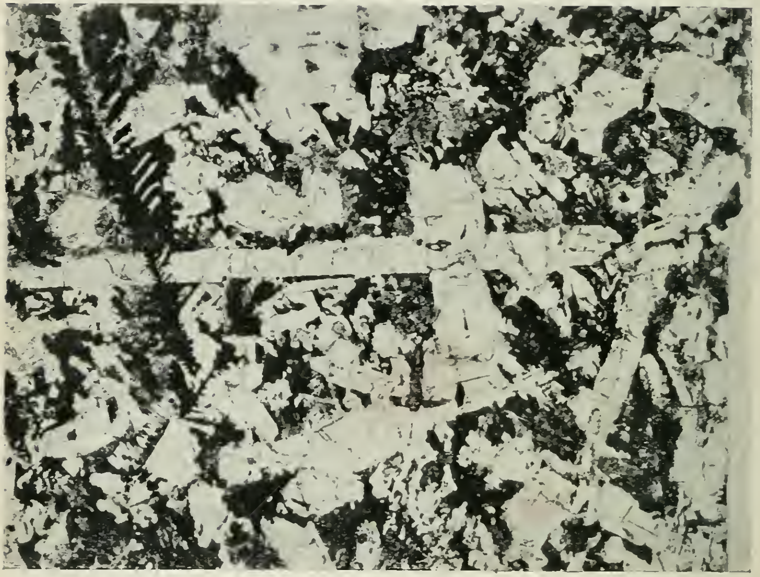

FIG. 22.—Photomicrograph of massive Basic Slag Crystals. White portion apatite, black ferns magnetic material, half-tone silicate possibly monticellite.

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Iron and Steel Institute.

REPORT OF THE INVESTIGATION INTO THE PROPERTIES OF REFRACTORY MATERIALS USED IN COKE-OVEN CONSTRUCTION.[1]

CARNEGIE RESEARCH GRANT, 1916–1918.

Carried out at the Imperial College of Science and Technology, South Kensington, S.W.

By WALTER C. HANCOCK, B.A. (Cantab.), F.I.C.

INTRODUCTION.

The investigation was undertaken at the invitation of the Iron and Steel Institute, to whom representation had been made that, prior to the outbreak of war, the bulk of the materials used in coke-oven construction had been imported from Belgium and Germany, and consequently a serious shortage was to be expected, as supplies from the former country were cut off owing to invasion, and from the latter as being an enemy country. Further, the economic importance of the coke-oven industry was increased by the war, as so many of the by-products are essential for the production of munitions of war.

The general scheme for the investigation, as originally suggested, was to obtain and examine specimens of coke-oven linings which had proved satisfactory in practice. It was proposed then to examine selected refractory raw materials of British origin which appeared likely to possess or to be capable of developing the qualities required for coke-oven linings. Apart from the chemical composition and such general physical properties as plasticity, texture, air- and fire-shrinkage, &c., the special qualities required for materials for coke-oven construction may be taken to be :

(1) Resistance to high and prolonged heating, under normal or increased pressure.

(2) Resistance to mechanical abrasion.

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[1] Report received August 1, 1919.

(3) Resistance to sudden changes of temperature.
(4) Impermeability to gases.
(5) Resistance to chemical attack, especially by sodium chloride at high temperatures.

The first step taken was the collection of information from manufacturers of coke-oven plant as to:

(*a*) The properties required in such linings.
(*b*) The pre-war sources of supply.
(*c*) The British sources of supply.

At the same time they were invited to suggest any further points for investigation and to submit any samples of coke-oven bricks which had proved either satisfactory or not in practice, in order, in the latter case, that an attempt could be made to determine the cause of failure.

A letter on these lines was accordingly addressed to seven leading firms, which for convenience and obvious reasons may be referred to under numbers. All, with the exception of one, expressed willingness to help the investigation as far as possible, though several were unable to promise much owing to the depletion of their staffs. Only one firm took the view that they could not supply information, which they conceived might subsequently be utilised by their competitors, although it was made quite clear that any information supplied would be treated in strict confidence and nothing would be published in a report without previous consent and approval.

The gist of the replies was as follows:

Firm No. 1 replied that up to some years ago they built coke-ovens with materials supplied from Germany, but since then they have built a very large number of ovens with English-made bricks and kindly supplied the names of the firms from which they were obtained.

Firm No. 2 stated that their experience of English-made bricks some years ago had been most unfortunate, and naturally they hesitated to return to their use without a preliminary trial which they considered should be about two years' actual practice. They have usually advised the use of Belgian bricks from the Mons district, and so far as their experience has gone, no English bricks have proved as good.

Firm No. 3 considered that excellent refractory materials for coke-oven construction are produced in this country.

Firm No. 4 replied that their experience of the performance of British-made refractories had not been satisfactory.

Firms Nos. 5 *and* 6 could not at the time supply information owing to pressure of work.

It is clear from the above résumé (1) that a considerable diversity of opinion exists among coke-oven builders as to the performance of British-made refractories in practice, and (2) that this country was not entirely dependent upon foreign sources of supply. In this and subsequent correspondence these firms also very generously supplied many technical details which can be more conveniently grouped under their respective headings below.

CHEMICAL COMPOSITION.

Broadly speaking, the refractories employed in coke-oven construction fall into two classes :

(1) Silica Bricks.
(2) Fireclay Bricks.

(1) *Silica Bricks*—as ordinarily understood—are not as extensively employed in this country as in the United States. The reason for this is that the coals used for coking in this country are " washed " and contain a larger amount of water (say 10–15 per cent. as against 5 per cent. in the States), and experience seems to show that a more aluminous brick (fireclay) is more satisfactory in presence of the higher moisture, although silica bricks are superior in heat conductivity.

As examples of the composition of silica bricks, the following may be cited :

	English.	American.
SiO_2	92·85	94·06
Fe_2O_3	0·40	0·87
Al_2O_3	3·35	2·23
CaO	1·30	2·52
MgO	trace	0·15
K_2O	0·30	0·15
TiO_2	1·40	...
Loss on ignition	0·40	...
	100·00	99·98

(2) *Fireclay Bricks.*—The more aluminous or "fireclay" bricks used in coke-oven construction contain a higher proportion of silica than most ordinary fireclays and are usually made from a mixture of some highly siliceous material, such as ganister, with a high-grade fireclay. It is usually considered that in a brick of satisfactory chemical composition the silica should not be less than 80 per cent., the iron reckoned as ferric oxide should not exceed 2 per cent., and the alkali should be less than 1·3 per cent., and lime and magnesia only about 0·5 per cent. each.

The following table gives the percentages of the chief constituents of a number of coke-oven bricks:

	SiO_2.	Al_2O_3.	Fe_2O_3.	K_2O.
Belgian	79·40	18·68	1·30	0·11
,, (Escoyez) . . .	81·14	14·20	1·30	1·07
American	79·29	16·66	2·26	0·82
German	83·15	13·19	1·57	1·17
English (1)	81·27	16·24	1·44	1·05
,, (2)	84·52	13·39	1·16	0·43
,, (3)	79·80	17·02	1·35	0·90
,, (4)	81·40	14·00	1·44	0·61
,, (5)	81·39	15·79	1·44	0·70
Means . . .	81·26	15·46	1·47	0·76

MECHANICAL PROPERTIES.

Judging from the information received, the general views held by many of the coke-oven builders in this country are that although there are apparently excellent raw materials available here, the manufacture of the bricks is not controlled as rigorously as it should be, and guarantees as to quality, performance, and dimensions, furnished by German and Belgian manufacturers, are not obtainable here.

It may be mentioned that these views are to some extent supported by what appears to be a fact, as far as evidence is available, that English raw clays were exported to the Continent, and the fireclay bricks made partially or entirely from them were afterwards imported into this country.

In order to work satisfactorily in a coke-oven it is essential that the bricks should be well made to ensure homogeneity, freedom from air-spaces, &c., and to prevent warping and change of volume when heated.

One of the large users stipulates that the bricks shall show no warping or softening at 1200° C. (about Seger cone 6*a*). The actual fusing or softening point of the materials should not be less than about 1610° C. (about Seger cone 27) under normal pressure, though in the light of recent work it is not improbable that this might be reduced by about 200° C. under increased pressure.

Another important quality of refractory articles for coke-oven construction is that they shall be true to size and shape when made. This can only be ensured by homogeneity of the mixture, and care in moulding and firing. A divergence of about $1\frac{1}{2}$ per cent. from specified dimensions is usually allowed. Closely associated with this is the constancy of shape and volume of the materials when actually in use in the oven, which can only be secured by careful moulding and thorough firing to a temperature sufficient to ensure that the maximum contraction and denseness have been attained.

It appeared that coke-oven linings would be subjected to considerable abrasion during the introduction of the charge of coal, and the expulsion of the coke by the ram. It certainly does occur to some extent, but owing to the contraction of the charge in coking, is not as great as at first sight might appear. Nevertheless some experiments on this point were carried out.

VISIT TO MIDLANDS.

During July 1916 the author visited a number of coke-oven builders and others in the Midlands, who generously gave him every assistance from their experience of the working of coke-ovens and the behaviour of the various refractories employed, and arranged for him to visit installations actually at work. He also visited several of the leading fireclay manufacturers and discussed the problems with them, and one firm very courteously showed him over their works and pits. Some of the chief points arrived at from this tour were:

(1) A considerable number of coke-oven materials have been produced in this country from a date prior to the war.
(2) Though much of the information given was of a highly detailed character, all the firms approved of the scheme outlined in Professor Bone's letter of March 10, 1916, the replies to which have been already summarised above, and none suggested any further points for investigation beyond those contained in it.
(3) Most of the points referred to above on pp. 42 to 45 were further discussed.
(4) Great emphasis was laid by all on the importance of resistance to attack by salty coal.

In addition, some specimens of coke-oven bricks of English and Continental origin were secured.

Although the scheme originally outlined has been adhered to in the main, the course of the investigation and the relationship of the various points have been somewhat modified during the progress of the work, and may be grouped under the following heads:

1. Texture.
2. Abrasion.
3. Porosity.
4. Density.
5. Permeability.
6. Expansion under heat.
7. The action of "salty" coals.
    (*a*) Coal washing.
    (*b*) Experiments with fluxing agents.

Texture.

The size of grain of the particles of the raw materials—whether the ultimate mineral grains or the aggregates left after grinding—is important on account of the influence it exerts on the properties of the manufactured products. The main properties affected by grain size are :

(1) Fine-grained material generally is less refractory and more susceptible to chemical attack.
(2) Coarse-grained material resists sudden changes of temperature better than fine-grained.
(3) Grain size obviously affects porosity and permeability.
(4) According to some observers grain size affects heat conductivity.
(5) Fine-grained material appears to resist abrasion better than coarse-grained.

Although a good deal of information exists as to grain size of clays, &c., in the unfired condition, it is highly desirable that definite knowledge should be acquired of the texture of fired products. Comparatively little has been done in this direction, mainly on account of the experimental difficulties, since there is no method by which fired products can be disintegrated in the same way as a lump of raw clay. Any method of crushing would of course destroy many of the particles which it is desired to retain as individuals. The only method available seems to be microscopic examination of either (1) thin sections, such as those used in petrography, or (2) flat polished surfaces, similar to those used in metallography. The drawback to the former is the difficulty and expense of obtaining sections sufficiently thin to transmit either ordinary or polarised light. Specimens can be obtained fairly easily for the latter method, and the application of an aqueous solution of certain organic dyes helps to differentiate the particles.

In view of the effect of grain size on the working qualities of refractories several raw materials have been elutriated and graded into four fractions, as below :

Fraction.	Name.	Diameters of the Particles.
No. 1	" Clay Substance " . .	0·00 – 0·01 mm.
No. 2	" Silt "	0·01 – 0·025 ,,
No. 3	" Dust Sand . . .	0·025 – 0·040 ,,
No. 4	" Sand "	0·040 – 0·200 ,,

The following results were obtained:

Fraction.	1.	2.	3.	4.	5.	6.
No. 1	48·7	47·7	34·1	24·1	34·7	22·6
No. 2	12·5	10·6	7·5	7·5	10·8	8·8
No. 3	9·0	8·5	9·6	10·0	12·9	11·8
No. 4	29·8	33·2	48·8	58·4	41·6	56·8
	100·0	100·0	100·0	100·0	100·0	100·0

No. 1 is the Stourbridge clay which has been used in all the series of test-pieces made. The others were also from the Stourbridge district, and are merely quoted here as further examples.

By simple inspection of such figures as the above, it is not possible to see which of the clays is really the "finest"—that is to say, in which is the sum of the areas of all the particles the largest. A measure of the sum of the areas of all the particles is given by the Jackson-Purdy surface factor. The surface factors for the above clays are:

1.	2.	3.	4.	5.	6.
10,978	10,682	7957	6040	8298	5856

Incidentally it may be mentioned that, according to this method of computation, if the whole of a clay consisted only of particles none of which exceeded 0·01 millimetre diameter, the total surface factor for such a clay would be 20,000; and, on the other hand, if all the particles ranged from 0·04 to 0·2 millimetre diameter, the factor would be 830. Clay No. 1, which was used for all the test-pieces, may be considered a fairly fine-grained specimen.

As, however, refractory clay materials as actually used are not manufactured from plastic raw clay alone, but from mixtures of this with a plastic material or "grog," the effect of texture on the properties of the products is further complicated. The test-pieces were made of clay and grog, and these were first standardised as far as possible in the following way.

All the raw clay was ground to pass a sieve of 30 meshes to the linear inch.

The "grog" used in the experiments was some of the same Stourbridge clay which had been fired to a high temperature;

probably about 1400° C., and was crushed and graded in the following way :

A. Fine. All passed a 30-mesh sieve, but not a 60-mesh.

B. Medium. Passed a $\frac{1}{16}$-inch mesh and was retained by a 30-mesh sieve.

C. Coarse. Passed a $\frac{1}{8}$-inch mesh and was retained by a $\frac{1}{16}$-inch mesh.

The ratio of clay to grog was also varied as follows :

1. Clay . . .	80 per cent.	Grog . . .	20 per cent.
2. Clay . . .	60 ,, ,,	Grog . . .	40 ,, ,,

These amounts were all measured by weight. The " volume-weights " were :

Clay,	1000 c.c.,	weighed	1380	grammes.
Grog (A)	,,	,,	1390	,,
Grog (B)	,,	,,	1280	,,
Grog (C)	,,	,,	1250	,,

It was not found practicable with test-pieces of the size employed, viz., 10 by 2·5 by 2·5 centimetres, to incorporate grog exceeding $\frac{1}{8}$-inch in diameter, or in amount above the ratio 40 to 60.

The following series of test-pieces, numbering twenty-four in all, were made up :

1.	Nos.	1– 3.	Neat clay.		
2.	,,	4– 6.	Clay, 80 per cent.	Grog, 20 per cent.	(30-mesh)
3.	,,	7– 9.	,, 60 ,,	,, 40 ,,	,, ,,
4.	,,	10–12.	,, 80 ,,	,, 20 ,,	($\frac{1}{16}''$,,)
5.	,,	13–15.	,, 60 ,,	,, 40 ,,	,, ,,
6.	,,	16–18.	,, 80 ,,	,, 20 ,,	($\frac{1}{8}''$,,)
7.	,,	19–21.	,, 60 ,,	,, 40 ,,	,, ,,
8.	,,	22–24.	,, 60 ,,	,, 40 ,,	($\frac{1}{16}''$,,)

(Repeat of series No. 5.)

The requisite quantities of ground clay and grog for each series were thoroughly mixed dry and water added until the mass had been brought into the proper working condition and was then left for a time to mature. The test-pieces were moulded by hand in metal moulds and weighed at once and on successive days until constant in weight in air and then dried at 105° C. The difference between the original wet weight and the air-dry weight gives approximately the amount of " tempering water " present, and is calculated as a percentage. The pieces were subsequently fired to about 1000° C.

Without reproducing all the details of the experiments, the following table gives the mean results :

	Neat Clay.	Clay, 80 per Cent. ; Grog, 20 per Cent.			Clay, 60 per Cent. ; Grog, 40 per Cent.		
		30-m.	$\frac{1}{16}$″.	$\frac{1}{8}$″.	30-m.	$\frac{1}{16}$″.	$\frac{1}{8}$″.
Loss in weight, Air	13·54	15·73	15·42	13·86	15·82	13·11	11·44
,, ,, 105°	15·28	17·21	16·72	13·22	17·00	15·30	12·97
,, ,, 1000°	22·36	22·83	21·84	20·61	21·39	19·51	17·34
Shrinkage, Air	4·13	3·87	4·40	4·13	3·35	2·40	2·40
,, 105°	4·33	3·93	4·40	4·20	2·25	2·40	2·40
,, 1000°	5·10	3·97	4·40	4·20	2·35	2·40	2·40
Percentage of water when moulded, calculated on dry clay	18·0	21·0	20·1	19·4	20·0	18·0	14·9

The above results show that increased amounts of grog reduce the quantity of water required for moulding and also the air- and fire-shrinkage. Fine grog does not reduce shrinkage to the same extent as coarser material. Also it appears that test-pieces containing grog require more water than the neat clay. In the course of the measurements it was noted that the presence of grog increases the rate of drying and also tends to counteract warping. These results, of course, confirm the views generally held, but the reasons for making the experiments again in this investigation were firstly, to have as complete a record as possible of the constitution of the test-pieces, on which other determinations were made later, and secondly, because one charge that has been made against English refractory materials for coke-oven construction is that they are not true to size and shape, qualities that can only be ensured by the use of proper amounts of correctly graded grog.

Many fireclays do not contain enough silica to yield a product with about 80 per cent. of that constituent, and as that amount has been widely adopted as most suitable for coke-oven linings, it is necessary to employ a mixture of materials. From the published analyses collected on p. 44 the mean percentages of the main components are: Silica, 81·26 per cent.; alumina, 15·46 per cent.; ferric oxide, 1·47 per cent.; and potash, 0·76 per cent. A series of test-pieces approximating to this composition was made from a mixture of clay, grog, and siliceous material, the analyses of which were:

	Clay.	Grog.	Siliceous Material.
Silica	68·80	70·90	92·55
Alumina	22·66	25·18	3·53
Titanium oxide	0·50	0·55	...
Ferric oxide	0·67	0·74	2·07
Lime	0·85	0·94	1·08
Magnesia	0·11	0·12	0·35
Potash	1·53	1·70	0·56
Combined water	10·00	...	...

Three series of test-pieces were made from these materials, viz., the same Stourbridge clay as had been used in the other tests, some of the same clay, fired and used as grog, and the above siliceous material or ganister. The last-named material had a "volume-weight" of 1700 grammes per litre; 61·0 per cent. of it passed a sieve of 30 meshes to the linear inch, 10·0 per cent. passed a 60-mesh but was retained by a 30-mesh, and 28 per cent. was retained by a 60-mesh.

The composition of the test-pieces is given in the following table:

	Per Cent.	Per Cent.	Per Cent.
Clay	40	30	30
Ganister	60	50	50
Grog	...	20 (30-mesh)	20 ($\frac{1}{16}$″)

The chemical composition of these series, calculated from the analyses above, is:

	Per Cent.	SiO_2.	Al_2O_3.	Fe_2O_3.	K_2O.
Clay	40	25·5	9·1	0·26	0·61
Ganister	60	55·5	2·1	1·20	0·21
		81·0	11·2	1·46	0·82
Clay	30	19·1	6·7	0·20	0·50
Ganister	50	46·2	1·2	1·00	0·28
Grog	20	14·2	5·0	0·15	0·35
		79·5	12·9	1·35	1·13

The results of these tests were :

	Clay, 40 per Cent. ; Ganister, 60 per Cent.	Clay, 30 per Cent. ; Ganister, 50 per Cent. ; Grog, 20 per Cent.	
		Grog, 30-mesh.	Grog, $\frac{1}{16}$".
	Per Cent.	Per Cent.	Per Cent.
Loss of weight, Air . .	12·37	12·10	12·49
,, ,, 105° . .	13·39	13·02	12·92
,, ,, 1200° . .	16·82	16·20	15·96
Shrinkage, Air . .	2·87	2·07	1·33
,, 105° . .	2·87	2·07	1·33
,, 1200° . .	2·90	2·13	1·67
Percentage of water when moulded, calculated on dry clay, &c. . . .	15·25	15·47	15·00

Allowing for differences in the composition, these results are similar in general to those obtained with clay material.

ABRASION.

There is not very much information available on the subject of abrasion of refractory materials, especially at working temperatures. At first it seemed that resistance to abrasion might be an important property of coke-oven linings, but except for the action of the ram on the sole of the oven, there is not much action on the walls on account of the shrinkage of the charge. However, a good deal of experimental work was carried out on this point which may be briefly recorded.

Three methods of measuring abrasion have been used :

1. The Bauschinger grinding machine.
2. The "wearing" test.
3. The "Rattler" test.

In the first, the test-piece is held against a horizontal revolving disc which is dusted with emery. The loss in weight after a certain number of revolutions is taken as a numerical expression of the amount of abrasion.

In the second, the test-piece is subjected to a blast of sand of standard size of grain for a definite time.

In the third, the test-piece is subjected to the grinding action of a number of iron balls in a closed rotating cylinder, all details of construction of the apparatus being minutely specified. The method really amounts to treating the test-piece in a modified "ball-mill."

A different method of testing was devised in the present investigation. The principle consists in causing one test-piece to pass backwards and forwards over the surface of another. The lower test-piece is rigidly fixed and the upper one is caused to move to and fro by being firmly attached to one end of a metal rod, the other end of which is connected with an eccentric driven by a small electric motor. The steady horizontal motion of the rod is secured by passing it through guides. The loss in weight of the test-pieces is taken as a numerical expression of the amount of abrasion. The method has the advantages that (1) the wear is caused by actual abrasion and not by grinding or scouring; (2) by loading the moving arm, the pressure of the abrading surfaces can be increased; (3) by substituting say a block of iron or coke for the upper abrading piece, the action of different substances on the refractory material can be measured; (4) by fixing the lower test-piece in a furnace in such a position that both pieces work within the furnace, the abrading action at high temperatures can be actually determined.

Some experiments were made to test the method with the following results:

	After 1 Hour.	After 3 Hours.	After 8 Hours.	After 18 Hours.
Top brick lost .	0·16	0·33	...	...
Bottom ,, ,, .	0·14	0·32	...	...
Top brick lost .	0·11	0·19	0·26	0·50
Bottom ,, ,, .	0·11	0·18	0·24	0·51

From these figures it appears that when both surfaces are of the same composition the amount of abrasion is about the same for both, and that it is roughly proportional to the duration of the test. It must be pointed out that when fresh surfaces are employed, the amount of abrasion is at first relatively large, but subsequently settles down to a fairly steady rate. In order to compare results it is preferable to record the loss after a given number of strokes rather than after a certain length of time.

Some experiments were made to ascertain the relation of abrasion at ordinary temperatures as compared with that at high temperatures. The following may be cited:

		Percentage Loss in Weight per 10,000 Strokes.
Neat clay on neat clay at	20° C.	0·20
,, ,, ,,	950° C.	2·13
Ditto, another set	1100° C.	1·41

The following table shows the mutual abrasion between a neat clay surface on the one hand and on the other surfaces that are more coarse, both on account of the quantity and size of the grog particles. The results are expressed as ratios, the abrasion of the neat clay surface being taken as unity:

Neat Clay.	Clay, 80 per Cent.; Grog, 20 per Cent.			Clay, 60 per Cent.; Grog, 40 per Cent.		
	30-mesh.	$\frac{1}{16}$".	$\frac{1}{8}$".	30-mesh.	$\frac{1}{16}$".	$\frac{1}{8}$".
1	1·1	...	...	3·6	...	...
1	...	1·0	...	...	4·0	...
1	...	...	1·0	...	...	3·0

The following table shows the mutual abrasion between surfaces of the same texture and the effect produced as the texture becomes increasingly coarse:

1.	Neat clay on neat clay	1·0
2.	Clay, 80%; Grog 20% 30-mesh on Clay 80%; Grog 20% 30-mesh	1·1
3.	,, ,, Grog 20%, $\frac{1}{16}$" on Clay 80%. Grog 20%, $\frac{1}{16}$"	1·1
4.	,, ,, ,, $\frac{1}{8}$" ,, ,, ,, $\frac{1}{8}$"	1·3
5.	,, 60%; Grog 40% 30-mesh on Clay 60%; Grog 40% 30-mesh	1·3
6.	,, ,, Grog 40%, $\frac{1}{16}$" on Clay 60%, Grog 40%, $\frac{1}{16}$"	2·2
7.	,, ,, ,, $\frac{1}{8}$" ,, ,, ,, $\frac{1}{8}$"	2·3

These results indicate that fine-grained surfaces suffer less abrasion than coarse-grained, whether the coarser texture is due to increase in quantity or in size of the grog particles.

Nearly one hundred experiments were made on abrasion, ranging from about one to twelve hours in duration. It is not practicable to reproduce all the results in detail, but the following points may be mentioned in this connection. Apart from the influence of grog referred to above, the experiments showed that abrasion seems to increase at high temperatures; that test-pieces fired to a high temperature were less abraded than similar pieces that had not been fired so hard, and that naturally abrasion is increased by the addition of load to the wearing surfaces.

Some experiments were also made with the test-pieces described above, made from clay ganister and grog. On the whole, the amount of abrasion with these was relatively small, and suggests that possibly to improve the quality of resistance to wear and tear, some advantage may be gained by the proper selection and mixing of suitable raw materials.

It may be of interest to note the results of an experiment made at ordinary temperature, in which the abrading piece was a block of iron, of the same size and shape as the neat clay brick abraded. The loss in weight of the latter was only 0·023 per cent. after 10,000 strokes and under a load of about a quarter of a kilogramme (say $\frac{1}{2}$ lb.).

POROSITY.

This property is important in connection with many qualities of refractory materials. It is really the total volumes of voids or pores expressed as a percentage of the total volume of the test-piece. This latter is often taken in one of two ways, either as the volume of the solid matter in the specimen plus the volume of the pores, or as the volume of the solid matter alone. According to S. Wologdine and A. L. Queneau[1] porosity may be defined as the volume of the pores expressed as a percentage of the total volume or as the ratio of the difference between the weight of the dry specimen and the specimen saturated with water to the weight of the dry specimen multiplied by 100.

If, P_s is the weight of the dry specimen;
P_m ,, ,, ,, specimen saturated with water;
P_e ,, ,, ,, ,, immersed in water;
then, $P_m - P_s$ is the volume of the pores;
and $P_s - P_e$,, ,, ,, matter without pores.

According to the first definition, the porosity (P_v) is:

$$P_v = \frac{(P_m - P_s) \times 100}{(P_s - P_e) + (P_m - P_s)}$$

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[1] *Electrochemical and Metallurgical Industry*, October 1909.

and by the second definition the porosity (P_p) is:

$$P_p = \frac{(P_m - P_s) \times 100}{P_s}.$$

The specimens were dried to constant weight at 105° C. They were then immersed in distilled water in a beaker and boiled to expel all the enclosed air, and the beaker and specimens were allowed to cool under reduced pressure. If on a second boiling no air bubbles appeared, the specimens were weighed, after cooling, on a hydrostatic balance. The specimens were removed from the water and weighed in a weighing-bottle after the superficial water had been removed by means of blotting-paper. These weighings give P_s, P_c, and P_m respectively.

DENSITY.

The "true" and "apparent" densities can be calculated from the values of P_s, P_c, and P_m by means of the following formulæ:

$$\text{True density} = \frac{P_s}{P_s - P_c}$$

$$\text{Apparent density} = \frac{P_s}{(P_s - P_c) + (P_m - P_s)}.$$

$$= \frac{P_s}{P_m - P_c}$$

The following table gives the results obtained with the neat clay and clay and grog specimens described above:

	Porosity.		Density.	
	P_r.	P_p.	True.	Apparent.
Neat clay	26·65	13·86	2·62	1·92
Clay, 80% ; Grog, 20% (30-mesh) .	26·92	14·31	2·58	1·89
,, ,, ,, ,, ($\frac{1}{16}$-inch mesh) .	26·35	12·96	2·59	1·90
,, ,, ,, ,, ($\frac{1}{8}$,, ,,) .	25·65	11·81	2·61	1·94
,, 60% ,, 40% (30-mesh) .	29·05	15·83	2·59	1·84
,, ,, ,, ($\frac{1}{16}$-inch mesh) .	26·87	14·06	2·61	1·91
,, ,, , ,, ($\frac{1}{8}$,, ,,) .	22·81	11·49	2·57	1·98

From these results it appears that an increase in the size of the grog particles tends to decrease the porosity while the density shows a slight increase.

Permeability.

As permeability by gases is an important property of linings for coke-ovens, some experiments were made on this point with the test-pieces described above, the life history of which has been fairly closely given.

The method adopted was that of Wologdine and Queneau, (*vide loc. cit.*) and need not be described again here. Essentially, it consists in passing a measured quantity of air, under a known pressure, through a test-piece of known area and length; the test-piece being luted into a glass tube with paraffin. The permeability, v, measured in litres passing through 1 square centimetre per second, is given by the formula:

$$v = \frac{1000 \times g \times l}{t \times (p - p_0) \times 60 \times s}$$

in which—

g = volume of air in litres;
t = time in minutes;
p_0 = height in the manometer at atmospheric pressure;
p = „ „ „ pressure p;
l = length of test-piece;
s = cross section of test-piece.

The following results were obtained:

Neat clay	0·0022	litres per sec.
Clay, 80% ; grog, 20% ($\frac{1}{16}$-inch mesh) . .	0·00094	„ „
Clay, 60% ; grog, 40% „ „) . .	0·00023	„ „

In this connection, the following experiments may be mentioned in which the permeability was determined of some test-pieces (made for other experiments) composed of particles of uniform grades, obtained by elutriation:

Size of Grain.	Permeability.
0·0 – 0·01 mm.	0·0108
0·01 – 0·025 „	0·0183
0·040 – 0·20 „	0·0704

From these figures it appears that the finer particles give a lower value for the permeability of gases.

Two points should be borne in mind with regard to these experiments on permeability, first that Wologdine and Queneau have shown that the property varies along different axes in any one specimen, and second that the determinations were made at the ordinary temperature, and it is highly probable that the permeability would be different, presumably greater, at high temperatures. From some published data, it appears that the greater the density the lower the permeability to gases, so that the temperature of burning would have an effect on this property.

Expansion under Heat.

Some experiments were made on this point. An optical method was adopted. Two platinum pointers were attached near the ends of a test-piece which was heated by three Meker burners, free movement of the piece being secured by supporting it upon fused silica rods. The heated test-piece was arranged in the path of a beam of light from a projection lantern and the images of the two pointers focussed on to two scales placed at a fixed distance from the test-piece. As the brick expanded the distances through which the images of the pointers moved on the scales could be measured and from these observations the expansion of the brick determined, the temperature attained being recorded by a thermocouple. As a control of the method, the expansion of an iron brick of approximately the same size and shape as the test-pieces was determined and the result obtained was $12{\cdot}07 \times 10^{-6}$, as compared with a value given by Holborn and Day of $11{\cdot}90 \times 10^{-6}$.

The following were some of the results obtained:

	At 750° C. Per Cent.	At 950° C. Per Cent.	At 980° C. Per Cent.
Neat clay	0·33	0·70	0·74
		At 800° C. Per Cent.	At 900° C. Per Cent.
Clay, 80 per cent.; grog, 20 per cent. (30-mesh) . .		0·34	0·47
		At 860° C. Per Cent.	At 990° C. Per Cent.
Clay, 60 per cent.; grog, 40 per cent. ($\frac{1}{8}$-inch mesh)		0·40	0·46

Action of "Salty" Coals.

When this investigation was suggested, the question of resistance of coke-oven linings to chemical attack was set down as one point to be considered. Although none of the coke-oven manufacturers whom we consulted suggested any other points for investigation beyond those originally outlined, all unanimously emphasised the importance of the effect of "salty" coals, which is a problem of great complexity and one on which considerable diversity of opinion exists.

Quite apart from the resistance of coke-oven linings in particular to chemical attack, the whole problem of resistance of refractory materials in general is a subject of wide economic importance. It has attracted attention in the allied industry of gas manufacture, owing to the destruction of retorts, in the iron and steel industry, in cases of failure of blast-furnace linings, and in fact affects the use of almost all refractory materials, since in practice virtually all of them come in contact not only with any water-soluble salts admixed with the fuel, but also with the mineral matter that forms an integral constituent of the fuel.

In the present instance, attention is of course only directed to the case of resistance of coke-oven linings to the action of salty coal, though the results of the examination of analogous cases have been borne in mind for comparison.

A considerable amount of literature exists on the subject, some of which is not easily accessible, and about forty papers and communications have been consulted with the object of ascertaining the extent of existing knowledge on this point. The following brief résumé has been prepared as an attempt to summarise impartially the main views that have been put forward and to indicate the general outline of the problem. It is not intended in any way as a critical examination of the published matter, and therefore no reference has been made to individual authors or their views.

1. *Salts in Coal.*—So far as the action on coke-oven linings is concerned, the only salts of importance are mostly soluble in water, or at least are impurities mechanically admixed with the coal, as distinct from the actual mineral constituents inherent in the coal substance, or so intimately mixed with it as not to be removable by washing with water. Although washing does not remove all these salts from coal, it effects a considerable reduction in the amount present, with the result that a higher grade coke is produced, provided that the water used for washing is sufficiently pure. The chief salts extracted by washing seem to be the chloride and sulphate of sodium, though of course there are probably others.

Washed coals used for the manufacture of coke in this country generally contain about 10 to 15 per cent. of water when fed into the ovens, but in the United States the amount is smaller. This water appears to be a factor in the problem, as it may act as a vehicle by which salts are directly conveyed on to the heated face or into the pores of the oven wall, and it may also take part in, or be essential to, the chemical reaction between the salts and the refractory.

2. *Composition of the Refractory.*—The main constituents of the refractory that are most important in this question of destruction of the oven walls are silica, alumina, and iron oxide. Free silica, present as quartz in the clay or as added grog, may be attacked by sodium chloride, and consequently in this respect coarse-grained material would be more resistant. Silica, however, is also present, combined with alumina in the actual "clay substance," and here a reaction similar to that involved in the well-known process of salt-glazing would occur, though in this connection it must be remembered that the temperature involved in salt-glazing is probably higher than the normal temperature of an oven wall.

Some diversity of opinion exists as to whether the alumina of the refractory is attacked by the salt or not. Some authorities claim that siliceous bricks have proved more resistant than aluminous, but there are many factors to be taken into consideration in arriving at a decision on this point.

Iron oxide, under the conditions obtaining in an oven, may be converted into chloride and volatilised and carried further into the pores of the refractory, where it would exert a fluxing effect. Further, as reducing gases are present, the production of a ferrous silicate which is well known to have a strong fluxing effect must be taken into account.

3. *The Physical Properties of the Refractory.*—From the point of view of resisting attack these are of importance. In the first place linings with a rough surface or a loose and open texture would obviously be more susceptible to attack. It was mainly in this connection that a good deal of attention was given in the experimental work described to texture and its effects, particularly to the size of grain of the clay and the size and amounts of grog, density, and permeability, &c. Want of truth in size and shape

of the bricks, which has been complained of in some English-made materials, is important here, because accurately made bricks enable the wall to be built with smaller and more compact joints, thus avoiding cracks or open spaces that would favour attack by salt.

4. *Deposition of Carbon.*—Another factor in the destruction of oven linings appears to be the deposition of carbon in the pores of the refractory, arising from the decomposition of methane or other hydrocarbons.

Some experimental work has been carried out on the action of salty coals and falls mainly under two heads :

1. Experiments on washing.
2. ,, ,, certain fluxing agents.

1. *Experiments on Washing.*—Some coals supplied by firms engaged in the coking industry were ground until they passed a $\frac{1}{16}$-inch sieve and were rejected by a 30-mesh, and washed intermittently with hot water.

Coal No. 1 yielded 0·16 per cent. of solids containing 0·007 per cent. chlorine.
,, ,, 2 ,, 3·55 ,, ,, ,, 0·710 ,, ,,
,, ,, 3 ,, 1·25 ,, ,, ,, 0·560 ,, ,,

From these results it appears that the percentage of chlorine in the solids in No. 1 is 4·38, in No. 2, 20, and in No. 3, 44. Unfortunately there is thus no fixed relation between the total solids and the chlorine.

It was thought that some relation might be found between the total solids and the state of division of the coal. One hundred and fifty grammes were taken and crushed to about $\frac{5}{8}$ inch diameter and treated with hot water till no more solids were removed. The coal, after drying, was then broken up into the successive sizes given below with the following results :

	Total Solids.	Chlorine.	Chlorine as Percentage of Solids.
	Per Cent.	Per Cent.	
Fraction 1. $\frac{5}{8}$ inch diameter . .	0·288	0·096	33·3
,, 2. $\frac{1}{2}$ inch–$\frac{1}{8}$ inch diameter	0·113	0·040	35·4
,, 3. $\frac{1}{8}$ inch–$\frac{1}{16}$ inch ,,	0·109	0·044	40·4
,, 4. $\frac{1}{16}$ inch–$\frac{1}{30}$ inch ,,	0·122	0·052	42·6
,, 5. $\frac{1}{30}$ inch–$\frac{1}{60}$ inch ,,	0·164	0·070	42·9
Totals . . .	0·796	0·302	37·9

From the above it appears that when broken to about $\frac{5}{8}$ inch in diameter, the largest amount, about 36 per cent., of the soluble salt is extracted. The amount of chloride, presumably sodium chloride, increased with the fineness of division of the samples.

The following results were obtained with three other specimens of coal used for coking purposes. The coal was ground to pass a $\frac{1}{16}$-inch sieve and warmed on a hot plate with water for eight hours and the extracted matter determined. The coal was then treated in the same way for four hours and again for four hours, and finally thrown on a filter and washed with hot water till the washings gave no opalescence with silver nitrate solution. In this case, most of the chloride is washed out in the first treatment, viz., in A, 49 per cent.; in B, 48 per cent.; and in C, 73 per cent. The last figure may be accounted for partly by the fact that coal C contains nearly double the amount of chloride in A. The large amount of soluble salt extracted in the last operation is due to the more thorough washing on the filter and the finer state of division of the samples at this stage, due to the friction to which they had been subjected in the previous operations.

	Time in Hours.				Totals.
	8.	4.	4.	4.	
Coal A.					
Solids, per cent. . .	0·267	0·117	0·076	0·188	0·648
Chlorine, ,, . .	0·062	0·290	0·007	0·029	0·127
Chlorine as percentage of solids	23·2	24·8	9·2	15·4	19·6
Coal B.					
Solids, per cent. . .	0·199	0·141	0·094	0·212	0·646
Chlorine, ,, . .	0·025	0·015	0·004	0·007	0·050
Chlorine as percentage of solids	12·1	10·6	4·3	3·3	7·7
Coal C.					
Solids, per cent. . .	0·345	0·086	0·071	0·180	0·682
Chlorine, ,, . .	0·161	0·013	0·008	0·037	0·219
Chlorine as percentage of solids . . .	46·7	15·1	11·3	20·5	32·1

2. *Experiments with certain Fluxing Agents.*—The first series of experiments were made with the object of establishing whether, when heated in the presence of coal, alkali finds its way into

the refractory. Pieces of fireclay that had been fired to about 1450° C. were heated in a crucible with 10 grammes of various coals. At the end of three hours the contents of the crucible were taken out and the fireclay mixed with a fresh quantity of coal and reheated for three hours; this treatment was repeated again. Finally the fireclay was taken out, washed free from chloride, ground and analysed for the alkali content. The content of alkali in the original fireclay was 1·7 per cent., reckoned as potassium oxide. Four coals were experimented with, first in the raw state and second after washing. The following results were obtained (the percentages of K_2O given in the table are the percentages found in the pieces of fireclay after the above treatment in the presence of the four coals both before and after these had been washed):

	With Unwashed Coal. Per Cent. K_2O.	With Washed Coal. Per Cent. K_2O.
Coal No. 1 . . .	2·38	1·78
,, A	3·09	2·46
,, B	2·20	1·97
,, C	2·75	2·28

Some experiments were made with coals in the dry and moist condition in an attempt to see if moisture really favours the action of salt in attacking the refractory,

	Increase in K_2O Content.	
	Dry Coal.	Moist Coal.
Coal No. 1 . . .	1·77	2·43
,, A	0·89	1·04
,, B	0·59	0·68
,, C	1·04	2·25

These results seem to show that the presence of water favours the actual incorporation of alkali into the refractory.

In conclusion, the author wishes to express his thanks to the Governors of the Imperial College of Science and Technology for the facilities afforded for carrying out the investigation; to Professor W. A. Bone, D.Sc., F.R.S., for his advice and assistance; to Mr. W. E. King, A.R.C.S., A.I.C., who has carried out the experimental work, the total amount of which has been far larger than would appear from the somewhat condensed summary given in this report; and to all those gentlemen engaged in coke-oven construction and fireclay manufacture who have most generously supplied details and results from their practical experience.

Carnegie Scholarship Memoirs, 1920.]

Iron and Steel Institute.

THE RELATION OF HEAT-TREATMENT TO COLD-WORK IN HYPO-EUTECTOID AND EUTECTOID STEELS.[1]

By A. T. ADAM, A.R.T.C.
(Bruntons' Research Laboratory, Musselburgh, Scotland).

Objects of Present Research.

The author's experiments have been confined to the products of a wire-mill, and such forms of cold-work as punching, stamping, and tube-drawing have not been investigated.

In approaching the problems involved in wire manufacture he made a careful study of the procedure adopted in works' practice, and the experiments carried out for this research were selected with a view to clearing up some points which appeared somewhat vague and uncertain; to offer if possible an explanation of the processes, and to standardise to some extent the method of procedure as regards the heat-treatment of each class of steel in relation to the cold-work it is to receive.

The effect of heat-treatment and, incidentally, ageing after cold-work, has naturally an important bearing on the subject, and as the effects are not only of considerable importance practically, but also of great interest as tending to throw further light on the condition of cold-worked material, investigations on this point have been included.

In studying wire-drawing practice there are one or two points which at first sight strike the metallurgist as peculiar, and seem to be at variance with accepted theories. One of these is the temperature usually reached in the "Patenting" process. It has been stated that the "Patenting" process is similar to normalising, and that its object is to remove rolling stresses, to refine the grain, and to produce sorbite. It should perhaps be made clear at the outset that this process of heat-treatment is used only when it is desired to produce high tensile wire. All wire in which strength is of little importance, such as iron or mild steel wire, or high carbon tool steel wire which is subsequently hardened and tempered, is simply annealed between the various stages in drawing. These latter classes of wire are perhaps more clearly defined in the French "fils d'acier" or in the English word "filament"; while in designating the former class the word "wire" is more appropriate, implying as it does toughness.

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[1] Received April 6, 1920. The original MS. was accompanied by a series of curves and of photomicrographs, which have been filed for reference in the Library of the Iron and Steel Institute.

Returning then to the "Patenting" process we find several points worthy of investigation:

1. Is the high temperature employed justified, and, if so, why?
2. Why should the production of sorbite be preferred to pearlite?
3. If, as has been stated,[1] the effect of cold-work can be almost entirely removed by annealing wire at a temperature of 600° to 650° C., why should the wire manufacturer resort to the more troublesome and costly process of "Patenting" as an intermediate heat-treatment?

Considering these points, the author in 1913 thought that refining of the grain and the production of sorbite might best be fulfilled by oil quenching and reheating, and that if this were really the structure desired some of the alloy steels similarly treated should produce a better class of wire. Experiments carried out at that time soon proved the fallacy of this idea, and it was found that rods treated in this way could not be drawn into satisfactory wire if they received more than one or, at the most, two passes. The conclusion arrived at then was that refining of the grain was not one of the objects desired in patenting, but that a large grain size with a fine structure in the grain was to be preferred, and that the failure of the alloy steels to produce good wire was largely due to this. Subsequent experiments, however, seemed to indicate that this form of heat-treatment might be usefully employed in the production of thick bars destined to receive not more than two light passes in drawing where good physical properties were required.

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[1] P. Goerens, "The Influence of Cold-Working and Annealing on the Properties of Iron and Steel." *Journal of the Iron and Steel Institute*, 1911, No. III.

In order to confirm these conclusions this form of heat-treatment has again been tested in the present research.

In presenting the results of these investigations it was thought desirable to divide the paper into three main parts :

1. Heat-treatment in preparation for cold-work.
2. Heat-treatment after cold-work.
3. Heat-treatment and cold-work in relation to micro-structure.

For granting facilities to carry out this work the author wishes to express his indebtedness to Messrs. Bruntons, and to thank the management for permission to publish the results in full.

He also wishes gratefully to acknowledge the valuable help and advice received from Dr. McWilliam, who assisted him with much of the work in the first part of the paper, and finally to thank the Laboratory Staff, especially Mr. F. S. Merrils, for assistance with the microscopic work and elastic limit tests.

PART I.

HEAT-TREATMENT IN PREPARATION FOR COLD-WORK.

Description of Steels Used.

Most of the work has been carried out on two steels, one a basic open-hearth steel of the following composition :

Steel "A."

	Per Cent.
Carbon	0·44
Silicon	0·06
Manganese	0·82
Sulphur	0·036
Phosphorus	0·031

and the other an acid open-hearth steel of Swedish make with the following composition :

Steel "B."

	Per Cent.
Carbon	0·85
Silicon	0·12
Manganese	0·30
Sulphur	0·022
Phosphorus	0·020

The latter was chosen because its composition more closely approaches the theoretical composition of the iron-carbon eutectoid or saturated alloy, and its comparative purity tends to eliminate other factors than those under examination.

Other steels have been included in the tests and their compositions are given in the tables of their mechanical properties.

In the case of Steel " A " all the experiments were carried out on pieces from the same coil of wire. This is also true of the experiments on Steel " B " with one or two exceptions, where wire of different gauges had to be used.

Methods of Heat-Treatment.

Since it was desired to carry out the heat-treatment according to works' practice, the samples were, wherever possible, treated in the works' furnaces, the temperatures of which were carefully controlled by pyrometers. When treatment in the works was not practicable the samples were treated in the laboratory, care being taken to keep the essential conditions similar. In order to make quite sure that no appreciable difference in the results obtained was due to the treatment being carried out on the laboratory scale, in some cases one or two samples were duplicated, and heat-treated both in the works and in the laboratory, and in these cases no appreciable difference was found.

In the works method the sample of wire or wire rod is gradually heated to the maximum temperature. In the laboratory furnace the samples had to be raised a little more quickly to the maximum, and in this case the sample consisted of a coil about 20 feet long, sufficiently loose to permit free circulation of air on cooling.

After heat-treatment the samples were pickled in the ordinary way and drawn down to the desired size, a piece large enough for testing being cut off after each pass through the drawing dies.

Nature of Tests.

Since it is the question of heat-treatment rather than the properties of cold-worked material that is under investigation, the tests made are severely practical. The problem as to what mechanical tests should be made was very carefully considered at the outset. While it would have been undoubtedly more satisfactory to include such tests as elastic limit and elongation in all samples, the work involved would have limited the ground covered, and after due consideration it was decided to sacrifice those tests except in specific cases. The effect of cold-work on the elastic limit has been fully treated in the second part of the paper in relation to the effect of heat-treatment after cold-work. In that part also the percentage elongation and resistance to alternating bend tests have been considered.

The effect of cold-work on the percentage of elongation is, of course, to diminish it greatly, and on fine wires the only accurate method of measuring it is by the microscope. The elongation is, moreover, in the author's opinion, of less importance in determining the quality of a wire than reduction of area.

It was thought at first that considerable difficulty would be encountered in measuring accurately enough the percentage reduction of area without using a microscope, but this was found comparatively simple by using a good point micrometer fixed to the bench, and the results obtained were found correct when compared with the microscope method within ± 3 per cent.

The tension tests on the wires were all carried out on an Olsen machine, which could be made to act as a 1000-lb. or 10,000-lb. machine by altering the jockey.

The thick bars and stream-line wires were tested on a 50-ton Rhielé machine, which was operated by a hand-wheel in testing for elastic limit instead of by power.

The torsion tests, with one or two exceptions which are noted in the tables, were all carried out on the actual length of 100 times the diameter of the wire.

Details of Treatment.

Steel "A." 0·44 *per cent. Carbon.*

A coil was selected which had already been drawn without heat-treatment from No. 5 S.W.G. rod to No. 8 S.W.G. wire. As all gauge numbers given represent "Standard Wire Gauge" they are hereafter simply indicated by a number and the one letter "G"—thus 12-G. This, after due consideration, was thought to be a better starting-point in this steel than the hot-rolled rod, because "ripping," as it is called, represents ordinary practice, the object being to make the wire more uniform in diameter before heat-treatment.

Nine samples of this coil were heat-treated as follows:

Temperature in Degrees C.	Method of Cooling.
850	In air. In lead at 500° C. In oil and reheated to 600° C.
950	In air. In lead at 500° C. In oil and reheated to 600° C.
1050	In air. In lead at 500° C. In oil and reheated to 600° C.

The temperature of the lead and the reheating temperature of the oil-quenched samples were selected after some preliminary experiments, the results of which are detailed in Table I.

In order to test if the rate of cooling after quenching in lead had any influence, some of these preliminary samples were cooled in water. Only in one case did cooling in water appear to have any effect, namely, in the sample cooled from 950° C., in lead at 350°, and in this case the temperature of the lead is probably responsible. It was just about this temperature that the first signs of brittleness were noticed in quenching pieces of this wire. These tests show that above 350° C. the temperature of the lead bath has comparatively little influence so far as the mechanical tests are concerned, and it was decided to use a temperature of 500° C. in further experiments on this steel, although one piece quenched at 350° C. was drawn to 22-G., and on testing gave a maximum load of 180 tons per square inch, 22 per cent. reduction in area, and 18 torsions on 100 diameters.

The nine samples treated as detailed above were drawn down as far as possible, mostly to 22-G., and tested after each pass. The results of these tests are detailed in Table II.

Conclusions from Test on Steel "A."

The effect of temperature variation between 850° C. and 1050° C. is not very striking, but the results appear to indicate that with air-cooling the capacity to stand cold-work increases with the temperature; this also appears to hold with the oil-quenched specimens, but not with lead-quenching. In the latter series the lower temperatures appear to give better results. The differences due to temperature, however, are so slight, we may conclude that the safe working range of temperature in the patenting process is extremely wide. There are indications that the capacity to withstand cold-work is to some extent a function of the grain size; the failure of the oil-quenched series and the higher tenacity reached by the wire air-cooled from 1050° C. suggest this, but the lead-quenched series indicate that this is not the chief controlling factor.

As these points still seemed a little uncertain a further experiment was made with this coil of wire. Two pieces were put through the same furnace, at the same time, and under identical conditions, with the exception of the rate of cooling, one being cooled in air and the other in lead. The temperature of the furnace was recorded at 1000° C., and that of the lead bath at 550° C.

These pieces were pickled carefully and drawn by one man. It was hoped in this way to eliminate all other variable factors but the rate of cooling, and so obtain a clearer idea of its influence.

The results of the tests on these samples are given as Final Series A and B in Table II.

The mean test results of all the air-cooled and lead-cooled wires are also arranged at the end of Table II. From these the effect of varying the rate of cooling is made clearer.

Although some of the irregularities noted are due to slight errors in testing they are not entirely due to this, but to inequalities in the reduction per pass. Apart even from these two causes, however, perfectly steady increase in tenacity, &c., could, not be expected.

The superiority of the lead-cooled wire is seen by considering the reduction in area in conjunction with the tenacity.

Details of Treatment.

Steel "B." 0·85 *per cent. Carbon.*

In steel of this temper it is not usual to attempt drawing without previous heat-treatment, and when fine wire is to be produced from it the rod has to be patented and drawn to a size suitable for patenting a second or third time in order to obtain the desired mechanical properties in the finished wire. It was, therefore, more with a view to determining the correct procedure in this intermediate or final heat-treatment that the experiments on this steel were selected.

A coil of this wire rod in 4-G. was patented in the ordinary way by passing through a long furnace and cooling freely in air, the maximum temperature reached being 1050° C. This coil was drawn to 12-G. wire, a piece being cut off for testing after each pass.

As before, several preliminary experiments were made before selecting the temperatures for the complete tests. These were made on the 4-G. rod and on the 12-G. wire, and the results are given in Table III.

These preliminary experiments showed that the minimum temperature of the lead in quenching this steel should be 450° C., and that cooling in water after the lead had no appreciable effect. The wire cooled in lead at 600° C. did not differ in tensile strength from that quenched at 500° C. The wire annealed at 600° C. after drawing to 12-G. had approximately the same tensile strength as the wires quenched in lead between 450° C. and 600° C., but stood about three times the number of twists in 100 diameters. Annealed at 650° C., it was still softer. Oil-quenching and reheating gave unsatisfactory results. The wires cooled in air were slightly lower in tensile strength than those quenched in lead. Some of the latter gave low tests, but this was considered to be due to inefficient quenching.

As a result of these preliminary experiments the following series of treatments were selected for the complete investigation :

1. 4-G. rod heated to 1050° C., cooled in air, and drawn to 12-G. (This wire to be used for subsequent heat-treatment.)

2. 4-G. rod heated to 850° C., cooled in air, and drawn to 12-G. (Eventually drawn to 13½-G.)

3. 4-G. rod heated to 1050° C., quenched in oil, and reheated to 650° C., and drawn as far as possible.

4. 4-G. rod heated to 950° C., cooled in lead at 440° C., and drawn to 13-G. (See No. 10, Table III.)

5. 12-G. wire drawn from (1), heated at 950° C., quenched in lead at 500° C., and drawn as far as possible. (Actually drawn to 25½-G., 0·019 inch diameter.)

6. Same, quenched in lead at 600° C. and drawn to 22-G.

7. Same, cooled in air and drawn to 22-G. (In this experiment only the 12-G. and 22-G. wires were tested.)

8. Same wire annealed at 600° C. and drawn as far as possible. (18½-G.)

9. Same wire heated to 780° C., quenched in lead at 500° C., and drawn to 22-G.

10. Same wire heated to 1050° C., quenched in lead at 500° C., and drawn to 22-G.

11. Same wire heated to 780° C., quenched in oil, reheated to 600° C., and drawn as far as possible. (This was afterwards abandoned as useless for cold-work.)

12. Wire from three different coils, originally treated as in (1), but drawn to 8-G. only, then heated to 1050° C., quenched in lead at 600° C., and drawn to 17-G.

13. 8-G. wire from one of these coils, annealed at 900° C., cooled in furnace, and drawn as far as possible.

EXPERIMENTS ON OTHER STEELS.

In order to compare these tests on this steel with others, the following further experiments were carried out :

14. An acid open-hearth steel wire rod, 2-G., of British make, and of the following composition :

Steel "C."

	Per Cent.
Carbon	0·70
Silicon	0·10
Manganese	0·54
Sulphur	0·042
Phosphorus	0·037

was drawn without heat-treatment to 4-G. and treated similarly to Steel "B" (1) and (5).

15. An acid open-hearth steel wire rod, 3-G., of British make, and of the following composition:

Steel "D."

	Per Cent.
Carbon	0·77
Silicon	0·12
Manganese	0·79
Sulphur	0·027
Phosphorus	0·035

was drawn after ordinary patenting to:

(*a*) 7-G. wire, heated to 900° C., quenched in lead at 550° C., and drawn to 16-G.

(*b*) 10-G. wire, heated to 900° C., quenched in lead at 550° C., and drawn to 20-G.

16. An open-hearth steel wire rod, 4-G., of Swedish make, and of the following composition:

Steel "E."

	Per Cent.
Carbon	0·87
Silicon	0·12
Manganese	0·25
Sulphur	0·021
Phosphorus	0·021
Nickel	0·50

(*a*) Treated as Steel "B" (1), but broke up in drawing at first pass.

(*b*) Heated to 1050° C., quenched in oil, reheated to 650° C., and drawn to 9-G.

17. An open-hearth steel wire rod, 1-G., of Swedish make, and of the following composition:

Steel "F."

	Per Cent.
Carbon	0·80
Silicon	0·12
Manganese	0·40
Sulphur	0·048
Phosphorus	0·022

(*a*) Heated in 1-G. to 1000° C., quenched in lead at 500° C., and drawn to 11-G.

(*b*) Similarly heat-treated but in 1, 2, and 3 gauges, all drawn to 12-G., and tested before and after galvanising.

The results of all these tests are detailed in Tables IV. to VIII.

Conclusions from Results on Steels "B" to "F."

(1) Again it is indicated, as in the case of Steel "A," that the permissible range of temperature in patenting is extremely wide, and there are indications that one of the objects in patenting is to enlarge the grain rather than to refine it. Refining the internal structure of the grain but increasing the grain size is the object of the process. In short, it seems that good wire is produced from what would normally be an over-heated steel.

(2) With steel of eutectoid composition, however, there seems to be no advantage in patenting beyond 950° C.

(3) The improvement obtained by cooling in lead is even more striking in these steels than in the medium steel.

(4) The fine structure produced by quenching in oil and reheating is quite unsatisfactory for withstanding cold flow.

(5) Experiment 8 shows clearly that heating below the critical range does not remove the effects of previous cold-work, and this treatment cannot replace patenting.

(6) Ordinary annealing is not suitable as a heat-treatment operation prior to cold-working in this class of steel.

EXPERIMENT ON THICK BARS.

18. In order to test the behaviour of material of larger dimensions when subjected to cold-work, a bar $1\frac{1}{4}$ inch diameter of acid open-hearth steel of the following composition :

Steel "G."

	Per Cent.
Carbon	0·49
Silicon	0·13
Manganese	0·65
Sulphur	0·037
Phosphorus	0·039

was heat-treated in various ways.

As such material does not fall under the category of wire, and does not as a rule receive great reduction by cold-work, the operation of quenching in oil and reheating finds application here. The object of this experiment, however, was rather to compare the cold flow of pearlite and sorbite in two specimens of this bar under the most adverse conditions, than to treat the matter from the practical point of view.

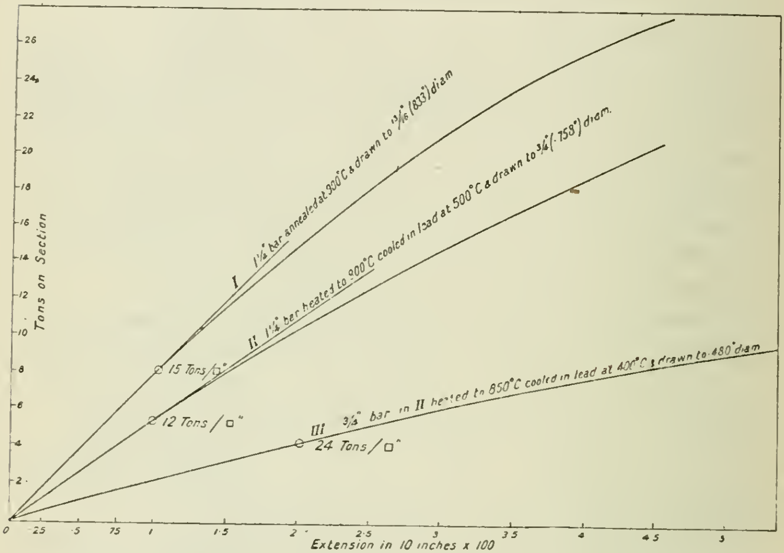

Fig. 1.—Elastic Curves of Tests on Thick Bars. Expt. 18, Part I., Table XIV., Steel G.

One specimen (*a*) was annealed at 900° C., the other (*b*) was simply patented at the same temperature.

The first piece was drawn to a $\frac{13}{16}$ inch diameter bar when it broke with a "cuppy" fracture. The second piece was drawn to $\frac{3}{4}$ inch diameter without fracture.

Tensile tests with the extensometer were made on the drawn bars, and the elastic curves are plotted in Fig. 1.

The $\frac{3}{4}$-inch bar was then divided into two parts: Part 1 was drawn without further patenting to 0·575 inch diameter without fracture, thus illustrating that a carbon steel in the sorbitic or patented condition is capable of withstanding cold-work to a much greater extent than in the pearlitic or annealed condition.

In the annealed condition fracture occurred after a reduction in area of 55 per cent., while in the patented condition a reduction in area of 79 per cent. was possible without fracture.

The other portion of the $\frac{3}{4}$-inch bar was repatented at 850° C. and drawn to 0·483 inch diameter.

Tensile tests on these bars were also made—on No. 2 with the extensometer, and on No. 1 without. A further test on No. 1 was made on a piece turned down to 0·342 inch diameter.

The results of all these tests are detailed in Table XII.

FATIGUE TESTS.

It was found possible at the last minute to carry out tests under alternating compression and tension on one of these specimens.

The bar chosen was No. 2 in Table XII., *i.e.* the $\frac{3}{4}$-inch bar. These tests were made on Dr. Haigh's alternating stress testing machine, which has been built at Bruntons' Research Laboratory. This machine is driven by a generator supplying 2-phase alternating current. The load is applied by electromagnets, and the generator provides one pair of alternations per revolution, one of each pair giving tension and the other compression. The speed of the generator is normally about 1000 revolutions per minute, thus giving about 2000 alternating stresses per minute.

The test-pieces for this machine have to be turned down to suit the load. In this case it was necessary to turn the $\frac{3}{4}$-inch bar down to 0·150 inch diameter, and since it cannot be assumed that cold-worked material is uniform throughout the section, the fatigue limit, as determined by these tests, can be considered only as an approximate figure.

It was in order to form an idea how the removal of the outer portion of the bar affected the test that one of the specimens in the ordinary static test was also turned down. A specimen of the $\frac{3}{4}$-inch bar was not available for this, but the 0·575 inch diameter bar was used, and the result is seen in Table XII.

In the fatigue tests the first specimen was tested under a load of 26 tons per square inch in compression and in tension, and broke after 41,000 reversals; the second piece was tested with a load just below the elastic limit as found by the extensometer, namely, 11·3 tons per square inch compression and tension. This specimen stood over 3,000,000 reversals. The load was then raised gradually on the same specimen to 13·7, 16·8, and 20·1 tons per square inch respectively. In each case it stood over 3,000,000 reversals, but broke in the last test after 3,092,000, indicating a fatigue limit of about 20 tons per square inch, or roughly 25 per cent. of the maximum load.

While it would be unsafe to draw any conclusion from this single experiment, it suggests that the fatigue limit of cold-worked material may possibly be above the elastic limit of the static test. A long series of tests on specimens which had not been turned down would be required to confirm this.

As the fatigue limit is in a sense the true elastic limit, a thorough investigation of this point would yield valuable information.

PART II.

HEAT-TREATMENT AFTER COLD-WORK.

Introductory Remarks.

The effect of heat on cold-worked material has to be considered in connection with such operations as hot-galvanising and tinning, where one is restricted to certain ranges of temperature. It is also worthy of study on a wider range from the point of view of its application as a heat-treatment operation solely and finally as a method of investigation on the condition of cold-worked material. For example, heat-treatment experiments on a faulty wire frequently give an answer to the question as to whether the fault is in the metal or alloy, or due to improper treatment in drawing.

General Heat-Treatment after Cold-Work.

The hardness and high tensile strength of cold-drawn steel wire, with the corresponding low power of elongation, is now largely considered to be due to the presence of amorphous or vitreous material. This amorphous "phase," as it has been called, is held to be in an unstable condition, but is prevented from returning to the stable or crystalline condition by the rigidity of the metal in the cold state. Ageing is said to effect a partial return, but if the metal be rendered less rigid by the application of heat this amorphous material will return to the crystalline condition to a greater or less extent, according to the temperature; thereby decreasing the hardness and tenacity of the steel—although at first there is actually an increase—but increasing the ductility, and possibly its power of resisting shock and vibration.

For this reason it has been thought that wire for certain purposes, such as aircraft tie-rods, would be improved by heat-treatment after cold-work, and in order to determine the effect of such treatment many experiments were made at Messrs. Bruntons during the war. Since the experiments carried out on this point for the present research are largely of a confirmatory nature, it has been thought advisable to refer to the earlier work, and in certain cases to give the actual test results. This work is described under the heading of "Preliminary Work."

Hot-Galvanising.

The evidence produced by practical experience shows that hot-galvanising has, on the whole, a deleterious effect on the physical properties of wire. The ductility, as represented by elongation, is increased, but the tensile strength is lowered, and if we take into consideration the number of twists and alternating bends the wire will stand before fracture, we find as a rule a decrease.

In order to illustrate this, three different classes of steel wire, at various stages in drawing, were galvanised under ordinary working conditions. The temperature chosen was 480° C., which is a fair average of the temperatures generally found in galvanising baths. The details of treatment and the test results are given in Table IX. These results, however, represent only one set of conditions, and even within practical working limits, such factors as temperature and time (or in the case of wire, speed) may vary considerably.

As it was inconvenient to vary these conditions in the works, the experiments which follow were for the most part carried out in the laboratory, and a lead bath was substituted for the zinc bath.

The wire chosen was a high tensile wire of about 12-G. It was drawn from a rod of the following composition :

	Per Cent.
Carbon	0·73
Silicon	0·15
Manganese	0·67
Sulphur	0·041
Phosphorus	0·036

In order to make sure that results obtained from a lead bath were comparable with those obtained from the zinc bath, the first two samples were treated in the galvanising bath at a temperature of 450° C.—No. 1 being held in the bath for thirty seconds, and No. 2 for fifteen minutes. The results of the tests on these wires are given in Table X., along with the results of the further samples of this wire heated in a lead bath for one minute at 350°, 400°, 450°, 500°, and 600° C. From these tests it is clear that time has an important influence on the result of the tensile test.

As an example of the disastrous effect of hot-galvanising on the resistance to torsion in certain cases reference is made to Table VIII., in which the results of tests on 12-G. wire drawn from Steel "F," treatment 17 (*b*), are given. In this case we are dealing with a steel which, although apparently quite satisfactory in composition, did not behave very well in drawing. (See Table VIII.) Before galvanising, the tests on this wire are fairly satisfactory, but the extremely poor result obtained in the torsion test after galvanising is probably due in part to a certain lack of homogeneity in the steel, as indicated in the drawing down.

It was suggested that these results might be due to the high carbon content, as works' experience seemed to indicate that wires containing more than 0·70 per cent. carbon did not stand hot-galvanising well. The author, however, was inclined to the view that the effect of galvanising under fixed conditions of temperature, time, &c., depended chiefly :

1. On the tensile strength of the wire, apart from carbon content.
2. On the homogeneity of the steel.

In order to test this point three wires of approximately the same gauge and physical properties, but one differing widely from the other two in carbon content, were galvanised at the same time and under exactly similar conditions. The wires were chosen from Steels "A" and "B," used in the first part of the research, and the results of the tests before and after galvanising are given in Table XI.

Conclusions.

These results indicate:

1. That hot-galvanising has a distinctly bad effect on the physical properties of wire, and, as a general rule, the higher the tenacity of the wire, however obtained, the more serious is the effect.
2. Time is an exceedingly important factor, especially as regards its influence on the maximum load. Its influence on the torsion test is not so striking.
3. Irregularities in cold flow are clearly revealed in torsion tests after hot-galvanising.
4. The temperature of the galvanising bath should be as low as possible, and the wire should be immersed in the bath for as short a period as possible, consistent with the production of a satisfactory coating of zinc.

Preliminary Work.

The Effect of Time in Heat-Treatment Operations.

If the increase in ductility is caused by a gradual transformation from an amorphous condition to a crystalline condition, one would expect time to play an important part. Thus in the tests carried out the time of heating was considered as important a factor as the temperature.

Details of Treatment.

Two series of wires were used, and in each series there were two sizes. The carbon content in Series A was approximately 0·45 per cent, and in Series B 0·70 per cent.

Series A consisted of wires having a tenacity of about 60 tons per square inch. These were divided into sets according to their sizes:

Set No. 1 . . .	0·140 inch diameter.
Set No. 2 . . .	0·185 inch ,,

Series B consisted of wires having a tenacity of about 100 tons per square inch. These were divided into two sets according to their sizes:

Set No. 1 . . .	0·138 inch diameter.
Set No. 2 . . .	0·177 inch ,,

After treatment the wires were tested for tensile strength and elongation per cent. on a length of 2 inches, and the results are plotted in the curves shown in Figs. 2 and 3. The details of treatment are given in these charts, and each point plotted is the mean of three tests.

SUMMARY OF FURTHER TESTS ON SERIES B.

The Effect of Heat-Treatment on the Resistance to Torsions and Alternating Bends.

1. The effect of time having been already determined, the wires were merely heated for thirty minutes at each of the following temperatures, 400°, 450°, 500°, and 550° C. It was found that heat-treatment tends to reduce the number of bends and torsions which the wire will stand. The effect was most pronounced at 400° C.

2. The effect of heat-treatment on wires produced by cold-rolling was found to be similar to that on the drawn wires.

3. The effect of heat-treatment on wires produced by swaging. Heating for thirty minutes at about 500° C. reduces the tenacity of swaged wires to the same extent as drawn wires without the corresponding increase in elongation. The elongation is increased, but not to the same extent.

CONCLUSIONS.

There are several points of interest in these curves, which may be briefly noted here:

1. In any thermal treatment after cold-work between 400° C. and 600° C. the time factor is just as important as that of temperature for periods below fifteen minutes.

2. The effect of time gradually decreases after a period of about fifteen minutes in wires of these dimensions.

3. In each set there is a certain temperature below which heating beyond one hour has little or no effect on the physical

properties tested ; in the medium steels, Series A, this temperature lies between 500° and 550° C. ; in the higher carbon steels, Series B, it lies between 550° and 600° C.

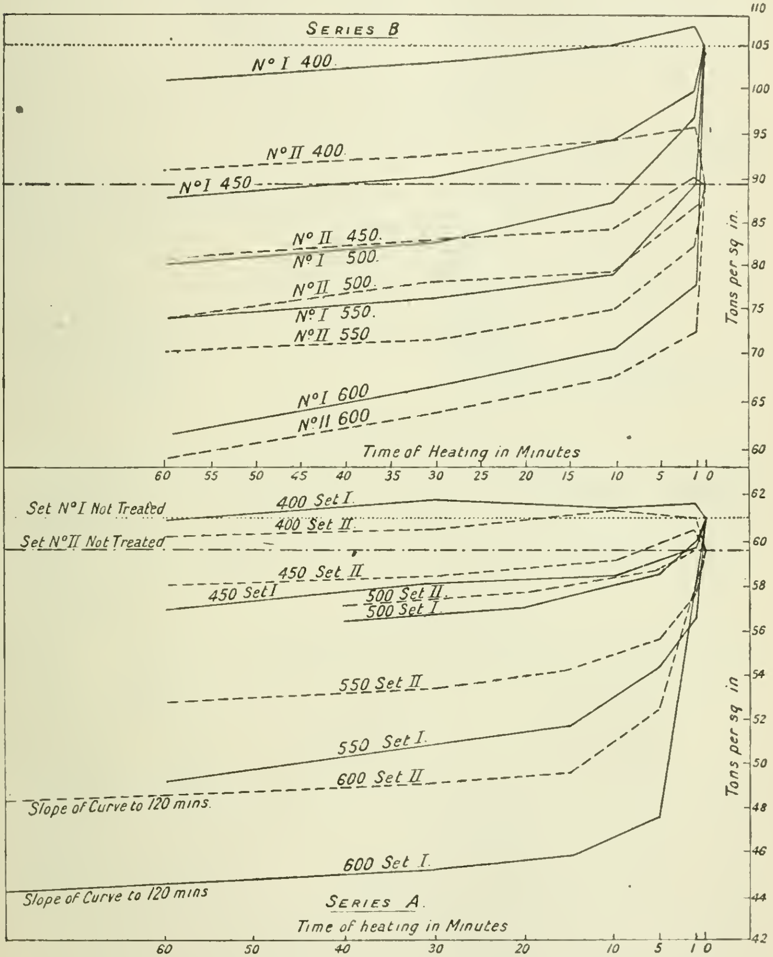

FIG. 2.—Effect of Time in Heating after Cold-Work on the Tenacity.

4. Above these temperatures a marked change takes place, in which time again has a distinct effect.

5. In Series A the effect of heat-treatment below the critical range appears to be almost complete after half an hour at 600° C.,

but in Series B it is not quite complete even after one hour at 600° C. It does not follow, however, that when, as has been suggested, such heat-treatment ceases to affect the physical properties, that the effects of cold-work have been removed.

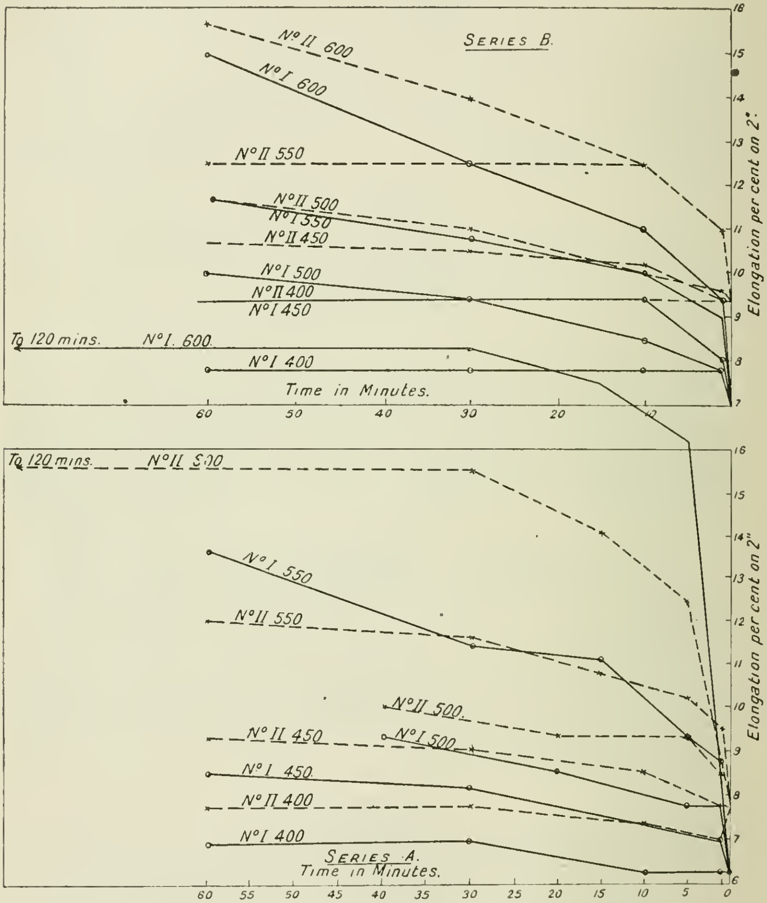

FIG. 3.—Effect of Time in Heating after Cold-Work on the Elongation.

6. Up to a certain point heat-treatment after cold-work increases the tenacity of the material.

7. Although such heat-treatment increases the ductility as represented by elongation, it has a deleterious effect on the resistance to alternating bend tests and torsions.

TESTS CARRIED OUT FOR PRESENT RESEARCH.

The previous experiments indicated that heat-treatment below 400° C., instead of softening cold-worked material, had rather a hardening effect, and it was in order to find the effect of low temperature annealing that these further experiments were done. The effect of ageing was also included.

For these tests two sizes of wires were taken; these were cold-rolled from $\frac{1}{4}$-inch and $\frac{1}{2}$-inch rounds to a sectional area of 0·0249 square inch and 0·1263 square inch respectively.

The compositions of the steels used were as follows:

	$\frac{1}{4}$ Inch. Per Cent.	$\frac{1}{2}$ Inch. Per Cent.
Carbon	0·42	0·48
Silicon	0·17	0·17
Manganese	0·73	0·68
Sulphur.	0·033	0·047
Phosphorus	0·029	0·025

All the specimens of each size were taken from the same length of wire; all the heat-treatment was carried out within a few hours of rolling, and one-half of the whole set was tested within a week of rolling; the other half was allowed to age for six months.

The temperatures chosen for heat-treatment were 100° C. and 350° C. The extensions in the tensile tests were measured by means of an extensometer capable of being read to $\frac{1}{10000}$ inch.

From these results the modulus of elasticity was calculated. The same readings also served to indicate the elastic limit.

A series of bend tests were made, the wires being bent round a certain radius, first through an angle of 90°, and then reversed through 180°, and so on till fracture occurred. The radius used for the $\frac{1}{4}$-inch wires was 0·480 inch, and for the $\frac{1}{2}$-inch wires 0·550 inch; in the latter case every half bend through 90° was counted.

The results of the tensile tests on the $\frac{1}{4}$-inch wires are plotted in Fig. 4, with a table giving the detailed figures, and the average results of the bend tests are plotted in Fig. 5, each point plotted being the mean of at least four tests. The tensile tests on the $\frac{1}{2}$-inch wires gave similar results.

In some of the $\frac{1}{2}$-inch wires heated to 350° C. the specimen was so brittle that it snapped immediately in bending. It was noticed

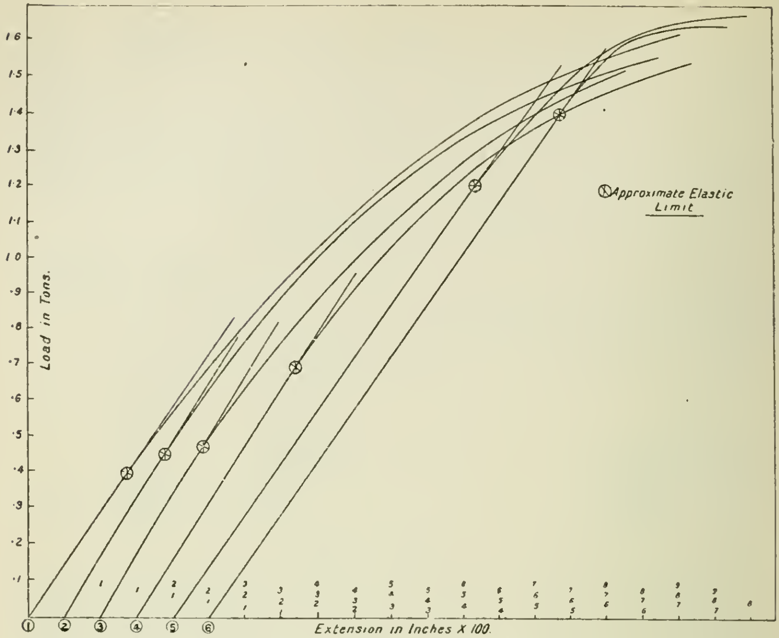

FIG. 4.—Stress-strain Curves of Streamline Wires rolled from $\frac{1}{4}$-inch Rod.

No.	Treatment.
1	As rolled.
2	Aged 6 months
3	Heated to 100° C.
4	Heated to 100° C., and aged 6 months
5	Heated to 350° C.
6	Heated to 350° C., and aged 6 months

No.	Area in Inches.	Elastic Limit in Tons per Sq. In.	Modulus in Tons per Sq. In.	Breaking Load in Tons per Sq. In.	Bends.	Elastic Limit. Extension per Cent. on 10 Ins.
1	0·00249	16	11,000	70·7	29	0·137
2	0·00249	18	13,400	71·0	28·5	0·137
3	0·00249	19	13,400	71·0	28·1	0·140
4	0·00249	28	12,700	69·2	26	0·220
5	0·00249	48	11,500	72·0	23	0·420
6	0·00249	56	11,500	70·0	21	0·44

that the speed of bending seriously affected the untreated wires, but had no effect on the wires heated to 350° C. For example,

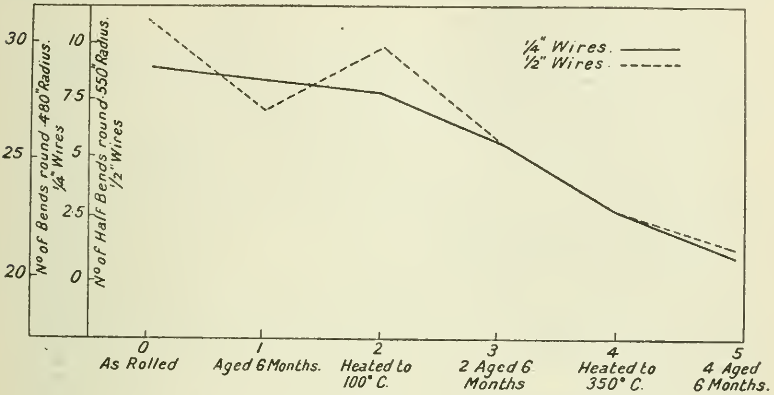

Fig. 5.—Average Results of Bend Tests on Streamline Wires after Heating and Ageing. Confirmatory Work.

the ¼-inch untreated wire stood 30 when bent slowly, but only 23 when bent very fast and locally heated.

Conclusions on the Effect of Heat-Treatment after Cold-Work.

The questions raised by the experiments in this part of the paper are somewhat intricate, and, since their true solution is important, they have naturally formed the subject of several investigations and have recently been widely discussed by men of great scientific repute. It is, therefore, with some diffidence that the author ventures into this torrid zone of controversy, and but for his confidence in the results of the tests, so far as they go, and the fact that they confirm more or less his general observations during the last six or seven years, he would keep to more temperate regions.

One of the main questions involved is the effect of cold-work on the elastic properties of steel, and as this forms the subject of a recent paper by Van Den Broek,[1] a comparison of the results and conclusions in both papers may be interesting. It must be remembered, however, that the specimens tested by Van Den Broek were of mild steel which had been cold-worked by straining, whereas the author's specimens were of medium steels which had been cold drawn or rolled.

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[1] "The Effects of Cold-Working on the Elastic Properties of Steel." *Iron and Steel Institute : Carnegie Research Memoirs*, 1918, vol. ix. p. 125.

1. Although a figure has been given for the elastic limit of these wires in the untreated condition it is almost impossible to say with certainty what the exact figure should be.

2. Heat-treatment and ageing after cold-work have a very pronounced effect on the elastic properties, and it would seem that the effect of ageing is actually greater on the heat-treated wires than on the untreated.

3. Even after boiling and ageing six months, however, the elastic limit of this wire is only about 40 per cent. of the ultimate load, while it rises to 80 per cent. after heating at 350° C. and ageing six months. It is this condition of maximum elasticity which really represents the climax of the hardening effect of cold-work.

4. The bend tests indicate that the recovery or increase of the elastic properties by heat-treatment and ageing is accompanied by an increase in brittleness.

5. These results, it is submitted, offer further support to the "amorphous cement theory" of cold-work, and seem to prove definitely the existence of some material in an unstable condition in cold-worked material. Immediately after cold-work this amorphous material is in a viscous or slightly mobile condition. The effect of time and heat is to change the viscous material to a vitreous and brittle condition. This change may be accompanied by a partial recrystallisation—indeed the formation of minute crystals or crystallites in the amorphous material would possibly account for the loss of viscosity—but the complete change seems to take place at a definite temperature somewhere between 500° and 600° C.

PART III.

HEAT-TREATMENT AND COLD-WORK IN RELATION TO MICROSTRUCTURE.

The conclusions drawn from the physical tests require some explanation, and it is to the microstructure that one naturally turns for this.

The microscopic study of wire presents probably greater difficulties than most forms of steel, because the whole structure is diminished in proportion to the reduction of the billet to the wire rod, and further because the chief constituent of properly heat-treated wires—viz. sorbite—is exceedingly difficult to resolve. For this reason most of the photomicrographs of wire which have been published tell us little beyond the fact that the crystalline grains are elongated by cold-work.

A short time ago the author was fortunate in securing a very good $\frac{1}{12}$-inch Zeitz oil-immersion achromatic objective with a numerical aperture of 1·3, which has enabled him not only to study specimens visually at magnifications of 1000 diameters, but to produce clear photographs up to a magnification of 2500 diameters, and in some cases as high as 5000 diameters with advantage.

At low powers the structures of the wires cooled in lead are scarcely distinguishable from those of the wires cooled in air, the only difference being a slight one in the amount of free ferrite visible. This difference is, of course, greater in thick rods than in thin wires. This point of distinction can be observed in hypo-eutectoid steels only. In wires of about 8-G. the difference is slight.

The effect of cold-work on the structure is seen in the photomicrographs which accompanied the original manuscript. Low power photographs show the general elongation of the grains after 1, 4, and 11 passes, that is, at 9, 13, and 22 gauges respectively, while the high power photographs reveal the differences in structure after lead cooling and air cooling and the effect of cold flow on the fine sorbite thus produced.

That cold flow in pure metals is due to slip along the crystal cleavage planes is now so widely accepted that it may be assumed here to explain the flow of ferrite. The flow produced by wire-drawing, however, differs from that of straining by direct pull. In the former case, the flow is due rather to radial stresses, the pull being sufficient not only to set up these stresses but to overcome the friction between the surfaces of the wire and the die. If the surface friction be too great the conditions may become momentarily those of direct tension, in which case, what is technically known as "sucking" will take place, *i.e.* the wire will be locally undersized and may break; or the material may yield too easily to the radial stresses and extrusion take place, resulting in ununiform flow and finally producing surface cracks. On the other hand, the surface may yield to the flow more readily than the interior, again resulting in irregular flow and finally in internal cracks, culminating in the "cuppy" fracture only too well known to wire-drawers.

The most striking difference in structure between a uniformly drawn wire and a piece of steel strained under direct tension, is that in the former the crystalline grains are elongated into fibres, with the grain boundaries for the most part unbroken, while in the latter the grains are ruptured at the weakest point before they become greatly elongated. A similar rupture may occur in a wire if an attempt is made to reduce it too much in one pass.

Cuppy fractures—apart from those produced in unsound steel—are not always accompanied by internal cracks, and in some cases microscopic examination failed to reveal internal fissures, or even much evidence of greater elongation of the surface grains, although it was clear from the nature of the fracture that the flow had been irregular. Such a case occurs in the $1\frac{1}{4}$-inch bar annealed and drawn to $\frac{13}{16}$ inch diameter (Experiment 18*a*, Part I.).

In this case the steel in the annealed condition consisted of pearlite and free ferrite in almost equal proportions, and in a bar of this dimension the flow at the surface tends to be greater than the flow at the centre. Thus internal rupture takes place. In a dead mild steel "hollow wire" is produced in this way by the formation of $<$ shaped cracks, which do not reach the surface owing to the rapid flow of the surface grains. Indeed such a case is illustrated by Goerens.[1] In the case of the steel containing pearlite, however, the surface flow is not sufficiently rapid to cover up the internal rupture and fracture occurs in a cuppy form as soon as the first crack develops.

When the structure is sorbitic, however, the flow is more uniform.

It would seem, therefore, that in drawing wire the lateral stresses must be sufficient to cause slip in the gliding planes throughout the whole section more or less uniformly without causing serious rupture at the grain boundaries, and the direct pull must not be greater than the yield point of the material.

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[1] *Carnegie Scholarship Memoirs*, 1911, Vol. III.

In soft metals, such as brass and mild steels, these conditions cannot be upheld in bars above a certain diameter, and such bars must be reduced gradually with frequent annealing. In annealed steels consisting of laminated pearlite and free ferrite the latter yields too readily for the former and irregular flow takes place. In such steels, however, which have been heat-treated so as to produce sorbite and little or no free ferrite, the flow is more uniform.

The questions now arise, how does cold-work affect the structure of a steel of eutectoid composition in the annealed condition, and why should sorbite flow more uniformly than laminated pearlite and even ferrite? It is of these problems that microscopic examination of wires at high magnifications seems to give a reasonable solution.

The structure of sorbite is for the most part granular or cellular, and although high magnification shows some signs of lamination, especially when cooling has not been sufficiently rapid, these are of a much finer nature than the laminations of pearlite. It is believed that these constituents are aggregates consisting of ferrite and cementite, which have separated from solution, and although the author is inclined to believe that complete separation has not taken place, yet even in sorbite particles of a hard white constituent, which may be assumed to be pure carbide—although unattacked by sodium picrate—are distinctly revealed by visual examination at a high power.

When laminated pearlite is subjected to cold-work, the flow or slip must take place in the direction of the laminations, and in many of the grains the direction of the laminations is opposed to the general direction of flow, hence great irregularity of movement must take place.

In sorbite, however, the hard constituent exists as small particles or thin plates intimately mixed with the soft iron, the whole structure being a fine network. The carbide exercises a restraining influence on the flow of the ductile constituent, while at the same time it is easily moulded, bent into line, or, if need be, broken by the flow of the soft iron by which it is enveloped. It is the necessity of moulding the whole internal structure to the line of flow that makes the movement in each grain more uniform and prevents the development of internal stresses and fissures.

The effect of cold-work on sorbite is to make what was originally a cellular structure or network become laminated in the direction of flow, and finally to cause the two constituents to become more or less separated or " divorced " from one another.

This separation was made quite evident by examination of highly drawn wires at high magnifications. It could also be noticed in etching such wires. A highly drawn wire did not darken so readily on etching as the patented wire. The constituents, however, were so minute that there was considerable difficulty in reproducing the divorced structure in photomicrographs, and it can really be made clear only in a wire that has been subjected to excessive cold-work.

With heat-treatment after cold-work there is no visible change in structure until a temperature of about 500° C. is reached. At this point the separation of the constituents of sorbite caused by cold-work becomes more pronounced, and after prolonged annealing below the critical range the complete separation or " divorce " is accomplished. The ferrite forms new grain boundaries and the cementite tends to coalesce into nodules. In this form it is attacked by boiling sodium picrate, but when separated by cold-work alone it is not. This suggests that the constituents of sorbite are not identical in composition to free ferrite and cementite.

The structure produced by annealing below the critical range after cold-work is in many respects similar to that produced by quenching and reheating, and both structures are unsuitable for withstanding cold-work. In mild steels (0·15 to 0·350 per cent. carbon) globular pearlite is produced by annealing below the critical range after cold-work, and in this condition such steels are surprisingly hard and tough and difficult to machine.

A bar of steel containing 0·30 per cent. carbon, which had been treated in this way, was tested and gave a maximum load of 42 tons per square inch, with percentage elongation of 21 on 2 inches. After annealing above the critical range the same bar gave only 28 tons per square inch maximum load, and 39 per cent. elongation. This tough condition of mild steels occurs frequently after hot-rolling at too low a temperature.

TABLE I.—*Steel "A." 0·44 per cent. Carbon. Drawn to 8 S.W.G. from No. 5-gauge Rod. Mechanical Tests after experimental Heat-Treatments as detailed.*

No.	Treatment.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Remarks.
			Lbs./Sect.	Tons per Sq. In.		
1	Heated to 1050° C. Lead-cooled at 500° C. . .	0·160	2410	53·6	45·7	Cooled in air after lead.
2	,, 950 ,, ,, 500 . .	0·159	2360	53·2	48·2	,, ,, ,,
3	,, 950 ,, ,, 400 . .	0·160	2582	51·5	44·6	Cooled in water after lead.
4	,, 950 ,, ,, 385 . .	0·160	2610	52·1	42·9	Cooled in air after lead.
5	,, 950 ,, ,, 350 . .	0·160	3422 4237	68·1 84·5	28·7	Cooled in water after lead.
6	,, 950 ,, ,, 350 . .	0·160	2510	50·0	50·9	Cooled in air after lead.
7	,, 900 ,, ,, 450 . .	0·157	2342	53·9	39·7	Cooled in water after lead.
8	,, 900 ,, ,, 450 . .	0·158	2348	53·6	43·1	Cooled in air after lead.
9	,, 900 ,, ,, 350 . .	0·161	2430	53·5	52·4	,, ,, ,,
10	,, 850 ,, ,, 550 . .	0·160	2395	53·4	56·0	,, ,, ,,
11	,, 1050° C. Oil-quenched at 600° C. . .	0·161	2760	60·6	50·1	
12	,, 950 ,, ,, 600 . .	0·160	2320	51·6	61·6	
13	,, 850 ,, ,, 600 . .	0·160	2480	55·2	54·4	

TABLE II.[1]—*Steel "A." Wire as received. 8-gauge ripped from 5-gauge Rod in two passes, about 25 per cent. reduction per pass.*

Chemical Analysis.	Per Cent.
Carbon	0·44
Silicon	0·06
Manganese . . .	0·82
Sulphur . . .	0·036
Phosphorus . . .	0·031

Mechanical Analysis.	
Diameter . .	0·162 in.
Maximum load .	88·2 tons per sq. in.
Elongation on 4 √A	13·4 per cent.
Reduction in area .	36·0 ,,

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.			Mean.	
			SERIES I.—*Heated to* 1050° *C. Air-cooled.*					
1	nil	0·161	2260	49·7	35	...	...	Elongation on 4 √A, 20 per cent.
2	26·5	0·138	2050	61·0	47	25, 18, 41	28	
3	23·3	0·121	1700	68·0	44	31, 32, 36	33	
4	23·3	0·106	1360	69·0	48	37, 38, 39	38	
5	23·2	0·093	1140	75·0	51	40, 38, 40	39	
6	31·3	0·077	830	80·0	40	35, 38, 41, 39, 38	38	
7	22·0	0·068	690	85·0	43	40, 40, 38, 33, 38	38	
8	24·6	0·059	540	89·0	53	37, 40, 40, 41, 37	39	
9	36·6	0·047	385	101·0	44	41, 34, 38, 42, 41	39	
10	34·6	0·038	285	111·0	36	37, 38, 38, 39, 39	38	
11	29·0	0·032	230	128·0	29	38, 36, 35, 39, 34	36	
12	29·0	0·027	200	156·0	29	34, 33, 36, 36, 38	35	
			SERIES II.—*Heated to* 950° *C. Air-cooled.*					
13	nil	0·161	2150	47·0	45	62	...	
14	27·5	0·137	1957	59·5	48	40	...	
15	19·4	0·123	1688	63·3	47	38	...	

16	28·5	0·104	1366	71·8	50	35	...	
17	22·0	0·092	1106	74·2	52	36	...	
18	28·0	0·078	843	78·8	45	38	...	
19	26·0	0·067	656	83·2	46	37	...	
20	30·0	0·056	529	96·0	49	37	...	
21	26·0	0·048	392	97·0	44	38	...	
22	...	...	...	...	...	...	...	Samples not cut off at this pass.
23	...	...	...	...	...	...	...	”
24	...	0·028	192	138·7	27	26	...	
Series III.—*Heated to 850° C. Air-cooled.*								
25	nil	0·159	2215	50·0	55	38	...	As patented.
26	29·0	0·134	1830	57·6	50	14, 20, 20, 22	19	
27	25	0·116	1480	62·3	50	23, 28	26·5	
28	29	0·098	1150	68·2	52	37, 40, 36	38	
29	28	0·083	930	76·6	53	37, 34, 38	36	
30	25	0·072	763	84·0	50	41, 41, 37, 36	39	
31	35	0·058	532	90·4	49	38, 39	38·5	
32	40	0·045	372	102·2	46	38, 38, 39	38	
33	39	0·035	254	118·0	36	27, 28	27·5	
34	36	0·028	180	131·0	26	25, 16, 24, 20, 18	20	Very irregular torsions.
Series IV.—*Heated to* 1050° *C. Lead-cooled at* 500° *C.*								
35	nil	0·160	2410 2170	53·6 48·2 } 50·9	46 41 } 43	54	...	As patented
36	21	0·142	1960	55·4	43	9, 11	10	
37	26	0·122	1620	61·7	39	7, 7	7	
38	25	0·106	1320	66·8	45	15	15	
39	26	0·091	1058	72·6	54	37	37	
40	36	0·0725	726	78·7	56	38	38	
41	22	0·064	602	83·6	55	39, 41	40	
42	23	0·056	487	88·4	54	41, 40	40·5	

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[1] Curves plotted from the figures in these tables accompanied the original manuscript, and these have been filed for reference in the Library of the Iron and Steel Institute.

Table II. (*continued*).

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.			Mean.	
43	32	0·046	354	95·2	55	43, 40	41·5	
44	35	0·037	270	112·1	33	39, 41	40	
45	25	0·032	221	123·3	39	35, 31, 36	34	
46	24	0·028	178	128·2	43(?)	32, 33	32·5	
Series V.—*Heated to 950° C. Lead-cooled at 500° C.*								
47	nil	0·159	2360 2320	53·2 52·3 } 52·8	52	23, 24	23·5	As patented.
48	22	0·140	2160 2160	62·5	49	40, 8	24	
49	25	0·121	1760 1690	68·2 65·5 } 66·9	55	22, 15, 47, 8	23	
50	22	0·107	1370 1440	68·1 71·5 } 69·8	57	37, 38	37·5	
51	25	0·093	1120 1130	73·8 74·4 } 74·1	58	31, 33	32	
52	30	0·078	862 865 } 864	80·7	56	40, 42	41	
53	24	0·068	710 712 699 708 } 707	87·0	57	38, 37	35·5	
54	26	0·0585	556 561 } 559	93·5	55	39, 40	39·5	
55	35	0·047	432 421 414 433 } 425	109·0	53	40, 39	39·5	

56	28	0·040	358 353 } 356	126·0	44	41, 38	39·5	
57	19	0·036	298 292 } 295	129·0	41	35, 38	36·5	
58	21	0·032	250 248 } 249	138·0	39	39, 33	36	
59	21	0·0285	218 213 } 216	151·0	36	39, 38	38·5	
60	29	0·024	163 159 154 162 157 152 } 157	154·9	38	26, 34, 34	31	

Series VI.—*Heated to 850° C. Lead-cooled at 500° C.*

61	nil	0·160	2395 2430	53·4 54·0 } 53·7	56 50 } 53	22	22	As patented.
62	29	0·135	2050	64·0	55	6	6	
63	27	0·115	1590	68·4	43	9	9	
64	24	0·100	1280	72·5	54	26	26	
65	27	0·0855	1056	83·0	55	33, 33	33	
66	27	0·073	797	84·7	57	33, 36	34·5	
67	37	0·058	552	93·5	52	36	36	
68	37	0·046	421	113·0	50	34, 24, 26, 36	30	
69	31	0·038	324	128·0	50	27, 32	29·5	
70	29	0·032	275	154·0	39	26, 27	26·5	

Series VII.—*Heated to 1050° C. Oil-quenched and Reheated to 600° C.*

71	nil	0·161	2760 2650	60·6 58·3 } 59·4	50 55 } 53	24	24	As treated
72	29	0·1355	2270	70·4	48	25, 26	25·5	
73	27	0·1165	1800	75·7	43	10, 27	18·5	

TABLE II. (*continued*).

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.		Bends.	Remarks.
			Lbs./Sect.	Tons per Sq. In.			Mean.		
74	23	0·102	1470	82·2	40	34, 35	34·5		
75	28	0·0865	1140	86·4	28	36, 33	34·5		
76	25	0·075	921	93·6	36	34, 33	33·5		
77	48	0·054	540	104·8	26	13, 14	13·5		
78	23	0·0475	439	112·0	13	5, 9, 15	9		
79	32	0·039	315	117–0	6	5, 11, 21	12		
80	35	0·0315	227·5	130·0	2	2, 14	8		
81	26	0·027	182	142·5	nil	1, 15	8		
SERIES VIII.—*Heated to 950° C. Oil-quenched and Reheated to 600° C.*									
82	nil	0·160	2320 2365	51·6 52·6 } 52·1	62 59 } 60	...	...		
83	30	0·134	2000	63·3	50	42, 45	43·5		
84	25	0·116	1680	70·8	45	46, 40	43		
85	22	0·102	1330	72·5	44	15, 11	13		
86	29	0·086	1230 (?)	93·0 (?)	39	12, 10	11		
87	24	0·075	822	83·0	36	21, 20	20·5		
88	48	0·054	498	97·0	25	21, 22	21·5		
89	53	0·037	280	116·0	15	7, 4	5·5		
90	25	0·032	148	82·5	nil	4, 3	3·5		
SERIES IX.—*Heated to 850° C. Oil-quenched and Reheated to 600° C.*									
91	nil	0·160	2480 2400	55·2 54·7 } 55·0	54 53 } 54	18	18		
92	28	0·136	2210	68·0	52	25	25		
93	24	0·1185	1820	74·0	47	12	12		
94	27	0·101	1400	78·0	28	8	8		

95	27	0·086	1078	83·0	39	12, 13	12·5		
96	25	0·074	861	89·5	33	20, 21	20·5		
97	43	0·056	582	106·0	8	7, 10	8·5		
98	32	0·046	404	109·0	4	2, 5	3·5		

FINAL SERIES "A."—*Heated to* 1000° *C. and Air-cooled.*

99	nil	0·1605	2220	49·0	53	...	...	...	
100	17	0·146	2030	54·2	47	53	...	6	
101	23	0·128	1740	60·0	48	32	...	6	
102	17	0·117	1570	65·0	43	27	...	8	
103	27	0·099	1240	72·0	53	37, 36	36·5	7	
104	34	0·080	901	80·0	50	40, 40	40	11	
105	28	0·068	682	84·0	48	43, 43, 43	43	16	
106	22	0·060	558	88·0	49	41, 41	41	19	
107	36	0·048	407	100·0	42	38, 38	38	18	
108	34	0·039	296	111·0	37	36, 37	36·5	18	
109	24	0·034	244	120·0	39	37, 37	37	24	
110	34	0·0275	185	139·0	40	29, 29, 31	29·5	10	

FINAL SERIES "B."—*Heated to* 1000° *C. and Lead-cooled at* 550° C.

111	nil	0·1605	2335	51·5	53	...	...	...	
112	19	0·144	2050	56·2	53	59	...	6	
113	22	0·127	1780	62·7	54	80, 66	73	7	
114	24	0·110	1380	65·0	56	41, 47	44	8½	
115	21	0·098	1220	72·0	55	38, 36	37	10	
116	36	0·080	897	80·0	54	40, 40	40	12	
117	27	0·068	697	86·0	54	45, 44, 44	44	15	
118	22	0·060	569	90·0	55	39, 41	40	24	
119	36	0·048	424	105·0	61	38, 38	38	28	
120	36	0·039	322	121·0	33	37, 37	37	34	
121	24	0·034	260	128·0	50	38, 39	38·5	28	
122	34	0·0275	202	151·0	40	30, 31, 33	31	36	

TABLE II. (*continued*).—*Average Results of all Air-cooled and Lead-cooled Wire.*

Air-cooled.					Lead-cooled.				
Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load. Tons per Sq. In.	Reduction in Area per Cent.	Torsions on 100 Diameters.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load. Tons per Sq. In.	Reduction in Area per Cent.	Torsions on 100 Diameters.
nil	0·160	49	47	...	nil	0·160	52	48	34
24	0·139	58	48	35	23	0·140	58	50	25
24	0·121	64	46	31	25	0·121	65	48	28
30	0·101	70	51	37	20	0·108	67	53	32
26	0·087	77	51·5	38	22	0·0955	73	55	33
30	0·073	82	45	39	31	0·079	80	56	38
30	0·061	88	49	38	40	0·061	89	55	40
35	0·049	100	45	38	40	0·047	105	55	38
33	0·040	109	38	35	35	0·038	123	40	36
46	0·0295	135·5	32	31	38	0·030	141	41	33·5

TABLE III.—*Steel "B."* 0·85 *per cent. Carbon. Mechanical Tests after experimental Heat-treatments as detailed.*

No.	Treatment.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Remarks.
			Lbs./Sect.	Tons per Sq. In.		
1	Heated to 900° C. Lead-cooled at 400° C.	0·223	Wire quite brittle.		...	Water-cooled after lead.
2	,, ,, ,, 450 ,,	0·223	6625	75·8	12·0	Air-cooled after lead.
3	,, ,, ,, 450 ,,	0·223	6338	72·4	22·6	Water-cooled after lead.
4	,, ,, ,, 430 ,,	0·219	6544	77·5	3·0	,, ,,
5	,, 950° C. ,, 440 ,,	0·220	5638	66·3	23·0	Air-cooled after lead.
6	,, ,, ,, 440 ,,	0·221	6320	73·4	19·6	Other end of No. 5.
7	,, ,, ,, 440 ,,	0·223	6710	76·7	21·0	Water-cooled after lead.
8	Nos. 5 and 6 drawn to 12-gauge . .	0·104 0·104	2080 2080	109·0	55·0	Torsions on 100 diameters, 42 and 43.
9	No. 7 drawn to 12-gauge . . .	0·105 0·105	2260 2340	117·0 121·0	Mean 50·4	Torsions on 100 diameters, 41, 43, 40.
10	Nos. 7 and 9 drawn to 13-gauge . .	0·092	2030 1900 1930 Mean 1953	136·0 127·5 129·5 Mean 131·0	43·8	Torsions on 100 diameters, 31, 35, 31. Mean 32.

TABLE III. (*continued*).

No.	Treatment.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Remarks.
			Lbs./Sect.	Tons per Sq. In.		
11	4-G rod as received . . .	0·228	...	53·6	42·5	Elongation per cent. on ½ inch, 22.
12	,, heated to 1050° C. and air-cooled .	0·225	...	63·0	24·0	,, ,, ,, 16.
13	12-G wire drawn from above . .	0·104	...	106·2	39·2	,, ,, ,, 8.
14	,, heated to 950° C. and air-cooled .	0·101	1244	69·4	...	Torsions on 100 diameters, 17.
15	,, ,, and lead-cooled at 400° C.	0·101	1510	84·3	...	Quite brittle.
16	,, ,, ,, ,,	...	...	...	...	Water-cooled after lead, quite brittle.
17	,, ,, ,, ,, 500° C.	0·101	1350	75·4	...	Torsions on 100 diameters, 12.
18	,, ,, to 1050° C. ,, ,,	0·101	1072 1138	57·3[1] 64·8[1]	31·2 24·2	Torsions on 100 diameters, 17 and 12.
19	,, ,, ,, 950° C. ,, 600° C.	0·101	1395	77·7	...	Torsions on 100 diameters, 10.
20	,, ,, ,, ,, ,,	0·101	1258	70·2	...	
21	,, ,, ,, 950° C. ,, 500° C.	0·101	1410	78·7	...	
22	,, ,, ,, 600° C. and air-cooled.	0·101	1338	74·5	...	Torsions on 100 diameters, 43.
23	,, ,, ,, 650° C. ,,	0·104	1042 1028	54·9 54·2	48·2 48·2	Torsions on 100 diameters, 74 and 76.
24	,, ,, ,, 1050° C., quenched and reheated to 600° C.	0·102	960 960	52·6 52·6	11·5 11·5	Torsions on 100 diameters, 8 and 12. Wire cracked.
25	,, ,, ,, 850°C., oil-quenched and reheated to 600° C.	0·101	830 840	46·3 46·8	13·5 15·4	Torsions on 100 diameters, 12 and 10.

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[1] Due to inefficient quenching.

TABLE IV.—*Steel " B." 4-Gauge Swedish Rod as received.*

Chemical Analysis.	Per Cent.
Carbon	0·85
Silicon	0·12
Manganese	0·30
Sulphur	0·022
Phosphorus	0·020

Mechanical Tests.	
Diameter	0·228 inches.
Maximum load	53·6 tons per sq. inch.
Elongation on ½ inch	22·2 per cent.
Reduction in area	42·5 ,,

EXPERIMENT I.—*Heated to 1050° C. and Air-cooled.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Elongation per Cent. on ½-Inch.	Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.				
1	nil	0·225	...	63·0	16·2	24	...	
2	31	0·187	...	79·0	16·0	27	36	Elongation and reduction in area lowered by patenting. Former decreased by cold-work, but latter raised.
3	19	0·169	...	82·6	14·0	18	39	
4	21	0·149	...	87·8	12·0	35	39	
5	27	0·127	...	96·6	10·0	43	40	
6	8	0·122	...	100·3	11·0	43	40	
7	27	0·104	...	105·9	12·0	48	37	12-gauge. Drawn from piece heated in laboratory.
8	...	0·104	...	106·2	8·0	39	39	

TABLE IV. (*continued*).

EXPERIMENT II.—4-*Gauge Rod. Heated to 850° C. Air-cooled and drawn to 13½-Gauge.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.			
9	29	0·1895	4930	78·0	27	By calculation :	
10	22	0·167	4190	85·0	29	18 on 8·35 = 36 on 100 d.	
11	21	0·1485	3530	91·0	38	17 on 7·4 = 34 on 100 d.	
12	26	0·127	2810 2840	99·8	15 42	14 on 5·7 = 31 on 100 d.	
13	19	0·114	2330	102·0	46	20 on 5·7 = 40 on 100 d.	
14	21	0·101	1950	109·0	43	37	
15	29	0·085	1550 1550	122·0	49	37 37	

EXPERIMENT III.—4-*Gauge Rod Oil-quenched at* 1050° *C. Tempered at* 650° *C. and drawn.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction of Diameter.	Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.				
16	26	0·193	4790	73·0	0·159	32	Not enough wire	Fracture flat and dark with silky edges.
17	18	0·175	4060	75·4	0·146	30	...	,,
18	13	0·163	3650	78·2	0·153	12	...	,,
19	26	0·140	3120	91·5	0·130	14	On 50 d. = 2 = 4 on 100 d. (woody)	,,
20	25	0·122	2610	99·6	0·113	14	On 50 d. = 2 = 4 on 100 d. (woody)	,,
21	27	0·104	2170	114·0	0·098	12	On 50 d. = 4 through marks repeated 10 = (8) and 20 on 100 d.	,,

TABLE IV. (*continued*).

EXPERIMENT V.—*Patented at 950° C. and Quenched in Lead at 500° C.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.		Mean.	
22	nil	0·098	1240	73·6	10, 28, 51	30	As patented. Note the irregularity in the number of torsions. This is due to severe local twisting.
23	23	0·086	1145 1145	87·4	43, 13, 50, 37	36	,, ,,
24	22	0·076	944 947	89·4	71, 68, 74, 71 53, 15, 48, 27	56	,, ,,
25	21	0·0675	771 771	96·3	61, 66, 66, 73 75, 73, 73	70	Torsions still local, travelling in some cases three times along the test-piece.
26	31	0·056	575 572	104·5	46, 38, 35, 39 73, 47, 61, 53	52	Torsions only partly local.
27	34	0·0455	437 428 424	115·5	48, 49, 52, 41	48	Torsions becoming more uniform.
28	34	0·037	325 327	134·8	42, 47, 43, 47	45	Torsions quite uniform.
29	25	0·032	278 270 273	152·0	35, 38, 41, 45	40	,, ,,
30	28	0·027	216 217·5	168·4	40, 41, 37, 38	39	Torsions quite uniform.
31	27	0·023	168·4 167·3	180·5	31, 28, 16, 37	28	Wire overdrawn. A small piece of this wire was drawn to 0·019 inch, and stood nearly 190 tons per square inch.

Experiment VI.—12-*Gauge Wire.* *Patented at 950° C.* *Quenched in Lead at 600° C. and drawn.*

No.	Reduction per Cent. per Pass.	Diameter Inches.	Maximum Load.		Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.		Mean.	
32	nil	0·101	1395 1258	77·7 70·2 } 74·0	10	10	
33	46	0·074	900	93·5	36, 30, 61	42	
34	27	0·063	711	102·0	50, 39	45	
35	29	0·053	553	112·0	38, 34	36	After testing in tensile, strained piece gave 40 torsions.
36	34	0·043	419	129·0	29, 36, 45, 32	36	Tensile piece gave 36 torsions.
37	22	0·037	325	134·0	36, 39, 38	38	
38	25	0·032	289	162·0	38, 41	40	
39	28	0·027	221	172·0	36, 45, 36, 38	39	

TABLE IV. (*continued*).

EXPERIMENT VII.—12-*Gauge Wire. Patented at* 950° *C. Air-cooled and drawn. As patented stood* 69·4 *tons per square inch and gave* 17 *Torsions.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. in.		Mean.	
40	...	0·027	185	144·0	39, 40	40	
EXPERIMENT VIII.—12-*Gauge Wire. Tempered at* 600° *C. and drawn. Would not draw beyond* 0·043 *inches or* 18½-*Gauge.*							
41	...	0·043	362	111·0	10, 7, 11	9	Test before drawing 74·5 tons per square inch and 43 torsions.
42	...	0·044	357	105·0	11, 14, 13, 13	13	
EXPERIMENT IX.—12-*Gauge Wire. Patented at* 780° *C. Lead-cooled at* 500° *C., and drawn to* 22-*Gauge.*							
43	21	0·089	1180	84·6	9	9	Low torsions in 43 and 44 due to severe local twisting; other test-pieces if available might have given more. *Cf.* Nos. 22 and 23 in this table.
44	29	0·075	893	90·3	17	17	
45	25	0·065	716	96·5	44	44	
46	28	0·055	590	111·0	37	37	Broke at grip.
47	33	0·045	426	120·0	39, 37	38	
48	29	0·038	327	129·0	34, 32	33	
49	24	0·033	251	131·0	37, 39, 40	38	
50	33	0·027	201 202	157·0	37, 36, 37	37	

EXPERIMENT X.—12-*Gauge Wire patented at* 1050° *C. Cooled in Lead at* 500° *C. and drawn.*

No.	Reduction per Cent. per pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.			Mean.	
51	nil	0·100	1072 1138	57·3 64·6 } 61·0	31 24	17, 12	14	This sample not efficiently quenched, hence low tensile tests on wire. Subsequent experiments on same steel heated to 1050° C. gave as good results as 950° C.
52	...	0·056	586	107·0	...	38, 35, 36	...	
53	...	0·046	400	108·0	...	33, 34, 43, 42, 50	40	
54	...	0·038	314 314	124·0	...	36, 38, 41, 34	37	
55	...	0·028	212 218 } 215	156·0	...	41, 41, 48, 44	43	
EXPERIMENT XII.—8-*Gauge Wire patented at* 1050° *C. Lead-quenched at* 600° *C. and drawn to* 17-*Gauge.*								
COIL 1.								
56	nil	0·160	3290	73·0	31	15, 9	12	As patented.
57	16	0·147	3160	83·0	43	37, 72	55	72, double twist.
58	22	0·130	2640	89·0	48	65, 17	41	65, ,,
59	19	0·117	2220	90·0	48	55, 48	52	Still local twisting.
60	21	0·104	1900	100·0	50	33, 39	36	Twisting more general.
61	22	0·093	1580	104·0	53	50, 35, 37	41	,, ,,
62	30	0·078	1200	112·0	48	39, 37	38	General twist.
63	28	0·066	960	125·0	48	32, 36	34	,, ,,
64	38	0·052	693	146·0	41	19, 19	19	Beginning to fail.

TABLE IV. (*continued*).

EXPERIMENT XII. (*continued*).

COIL 2.

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.			Mean.	
65	nil	0·160	3375	74·8	24	13, 7	10	As patented.
66	16	0·147	3240	85·5	32	38, 42	40	
67	22	0·130	2680	90·6	39	45, 15, 4	21	
68	18	0·118	2310	94·5	45	37, 37	37	
69	22	0·104	1920	100·9	45	44, 49	37	
70	22	0·093	1580	103·8	54	43, 35	36	
71	30	0·078	1260	117·9	50	35, 35	35	
72	28	0·066	970	126·6	38	34, 33	33	
73	38	0·053	730	148·0	28	22, 25	23	
					COIL 3.			
74	nil	0·160	3380	75·0	27	12, 6	9	
75	16	0·147	3250	85·8	34	12, 18	15	
76	21	0·129	2730	93·6	38	15, 39	27	
77	22	0·116	2280	96·8	41	54, 30	42	
78	27	0·099	1810	105·0	46	32, 33	33	
79	33	0·081	1360	117·8	45	25, 39	32	
80	27	0·069	1030	123·0	45	46, 36	41	

EXPERIMENT XIII.—*Annealed at 900° C.*

This wire before drawing had a tenacity of about 40 tons per square inch, with a good elongation, but a poor reduction in area. It broke after two passes in drawing to 0·127 inch diameter, and stood 60 tons per square inch, with an average of 6 torsions, and hardly any reduction in area.

TABLE V.—*Steel "C."*

Chemical Analysis.	Per Cent.
Carbon	0·70
Silicon	0·10
Manganese	0·54
Sulphur	0·042
Phosphorus	0·037

Mechanical Tests.	
Diameter	0·276 inch
Yield point	31·7 tons per sq. inch 35·0 ,, ,,
Maximum load	57·2 ,, ,, 57·8 ,, ,,
Elongation on $4\sqrt{A}$	18 per cent.
Reduction in area	35 ,,

EXPERIMENT XIV.—*For comparison with* 1 *and* 5. *Patented in Furnace at* 1050° *C. Air-cooled from* 5-*Gauge* (0·212 *inch*).

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Elongation per Cent. on 0·5 inch.	Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.				
1	nil	0·223	4900	56·0	...	...	...	As patented.
2	28	0·189	4300	68·5	14	22	29	
3	13	0·176	3940	72·3	14	27	33	
4	20	0·157	3370	77·9	14	26	29	
5	26	0·135	2655	83·0	14	30	22	
6	24	0·118	2160	88·5	10	28	26	
7	23	0·104	1710	90·0	...	...	25	

TABLE V. (*continued*).

EXPERIMENT XIV. (*continued*).—*Patented at 950° C. Cooled in Lead at 500° C.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.			Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.		Tons per Sq. In.		Mean.	
8	nil	0·101	1240		69·2	10, 10, 13, 13	12	
9	26	0·086	1061, 1060 1065, 1050	1059	81·4	42, 13, 12, 12, 12	18	
10	24	0·075	821, 866 832, 846	841	85·0	25, 56, 17, 41	35	
11	20	0·067	678, 696 692, 693 704	693	87·6	41, 42, 44, 45, 32, 29, 55	43	
12	34	0·0545	511, 538 527, 529 510	523	100·0	42, 42, 41, 40	41	
13	33	0·0455	381, 389 420, 400 400	398	109·6	40, 41, 42	41	
14	30	0·038	301, 302 309, 320	308	122·0	42, 42, 41, 40	41	
15	29	0·032	245·5 254·5	250	139·0	42, 36, 40, 39	39	
16	29	0·027	188·5 188·3, 202	192·9	150·0	37, 41, 36, 39, 28, 29, 29	34	22-gauge.

TABLE VI.—*Steel "D," with the following composition:*

	Per Cent.
Carbon	0·77
Silicon	0·12
Manganese	0·79
Sulphur	0·027
Phosphorus	0·035

EXPERIMENT XVA.—*3-Gauge Rod drawn to 7-Gauge Wire. Heated to 900° C. Lead-cooled at 550° C. and drawn to 16-Gauge.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.		Bends over 3 Diameters Radius.		Remarks.
			Lbs./Sect.	Tons per sq. In.		Mean.		Mean.	
1	nil	0·174	3960	74·0	29, 47, 12	29	10½, 10½, 12	11	
2	12	0·163	3800	81·0	12, 15, 46	24	12½, 16½, 14½	14½	
3	22	0·144	3280	90·6	27, 30, 22	26	12½, 12½, 14	13	
4	20	0·129	2760	94·6	13, 19, 36	23	18, 18, 18	18	
5	29	0·109	2130	102·2	32, 33, 32	32	20, 25, 18	21	
6	29	0·092	1695	114·8	33, 25, 27	28	...	...	
7	28	0·078	1300	123·0	25, 25, 25	25	...	...	
8	28	0·066	1025	134·5	25, 26, 27	26	...	...	

TABLE VI. (*continued*).

EXPERIMENT XVB.—*Same Rod drawn to 10-Gauge wire. Heated to 900° C. Lead-cooled at 550° C. and drawn to 20-Gauge.* Cf. *Experiment V., Table IV., Steel "B."*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load		Torsions on 100 Diameters.		Remarks.
			Lbs./Sect.	Tons per Sq. In.		Mean.	
9	nil	0·119	1990	80·0	2, 2, 2, other end 3	2	All bad fractures.
10	40	0·092	1160	78·0	36, 39, 38, 38	38	
11	24	0·080	1100	97·5(?)	37, 32, 21, 34	31	This test could not be checked.
12	19	0·072	840	92·5	32, 39, 39, 33	36	
13	21	1·064	688	95·5	37, 36, 40, 38	38	
14	26	0·055	546	102·5	39, 41, 38, 39	39	
15	36	0·044	409	120·0	37, 37, 37, 36	37	
16	29	0·037	337	139·0	19, (8), 22, 19	17	(S) gave a bad fracture (spiral)

TABLE VII.—*Steel "E."*

	Per Cent.
Carbon	0·87
Nickel	0·5

EXPERIMENT XVIB.—*Swedish Nickel Steel, 5-Gauge Rod. Oil-quenched at 1050° C. Tempered at 650° C. and drawn.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.			
1	27	0·191	4800	74·8	19	8	Fracture flat.
2	15	0·176	3090	62·0	2	4	
			3880	71·4	25		
3	19	0·158	3300	75·2	17	1	
			3360	76·5	13		
4	18	0·143	1810	50·2[1]	2	2	[1] Snapped.
			3410	94·6	15		

N.B.—This steel completely failed in drawing, but this is not necessarily due to the presence of nickel.

TABLE VIII.—*Steel "F."*

EXPERIMENT XVIIA.—*Swedish Steel, 1-Gauge Rod, patented at* 1000° *C. Lead-cooled at* 500° *C. Carbon,* 0·80 *per cent.*

No.	Reduction per Cent. per Pass.	Diameter. Inches.	Maximum Load.		Elongation per Cent. on 4 √A.	Reduction in Area per Cent.	Torsions on 100 Diameters.	Remarks.
			Lbs./Sect.	Tons per Sq. In.				
1	nil	0·266	9184	73·7	10·6	18	...	On tensile fracture. Dark core.
2	18	0·241	8646	84·6	2·3	6	...	,, ,,
3	22	0·213	6473	81·2	7·9	25	...	Clear.
4	18	0·193	5532	84·4	2·9	3	...	Cuppy.
5	13	0·180	5308	93·0	9·4	30	...	Clear.
6	21	0·160	4715	105·3	14·3	45	28 g. fract.	By lens fracture split radially.
7	18	0·145	3740	101·6	13·5	38	40 ,,	Same.
8	20	0·130	3396	114·7	13·0	35	37 ,,	Cuppy and cracks.
9	19	0·117	2710	113·6	14·3	47	33, 41 ,,	Cracks.
Same Steel from another Coil.								
10	nil	0·2665	9587	71·6		20	...	Frac. crys. bright grey.
11	18	0·241	8019	78·6		19	...	Same but no cracks.
12	22	0·213	6764	85·0		20	...	Nice silky fracture.
13	18	0·193	5689	86·6		14	...	
			5734	87·3				
14	13	0·180	5510	96·5		37	...	Perfect cup and ball.
15	21	0·160	4810	107·0		42	38 flat.	Cup and ball.
			4704	104·2				
16	18	0·145	3890	105·0		41	38 ,,	Radial cracks.
			4009	108·2				
17	20	0·130	3410	114·5		46	36 spiral.	,, ,,
			3470	115·6				
18	19	0·117	2840	117·0		46	33 flat.	,, ,,
			2870	119·2				

EXPERIMENT XVIIB.—*Steel "F." Before Galvanising. Patented in 1-Gauge and drawn 10 Holes.*

No.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.	Remarks.
		Lbs./Sect.	Tons per Sq. In.		
19	0·105	2480	128·0	29 on 8 ins.	
	0·106	2380	123·0	31	
20	0·105	2340	121·0	6	
	0·106	2360	120·0	31	
21	0·106	2480	126·0	24	
	0·106	2440	124·0	28	
		Means 2413	124·0	25	Before galvanising.
		2241	112·0	6	After ”
Down 7 per cent. in lbs. and 9 per cent. in tons. These numbers are not the same owing to difference in diameters.					
Patented in 2-Gauge and drawn 9 Holes.					
22	0·105	2260	117·0	31 on 8 ins.	
	0·106	2360	120·0	31	
23	0·105	2340	121·0	32	
	0·106	2380	121·0	32	
		Means 2238	120·0	32	Before galvanising.
		2158	107·0	3	After ”
3·6 per cent down in lbs. 10·8 down in tons.					
Patented in 3-Gauge and drawn 8 Holes.					
24	0·106	2400	122·0	30	
	0·106	2280	116·0	30	
		Means 2340	119·0	30	Before galvanising.
		2205	108·0	2	After ”
Down 5·8 per cent. in lbs. and 9·2 per cent. in tons.					

TABLE VIII. (*continued*).

No.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.	Remarks.
		Lbs./Sect.	Tons per Sq. In.		
Tests after Galvanising. Temperature 420/50° C. Patented in 1-Gauge 10 Holes.					
25	0·106	2320	118·0	4	25 and 25A are the same piece broken in two.
	0·106	2230	113·0	5	
25A	0·106	2180	110·0	3	
	0·107	2240	111·2	9	
26	0·107	2210	110·0	5	
	0·109	2260	108·0	1	
27	0·106	2300	117·0	7	
	0·106	2190	111·0	5	
Patented in 2-Gauge and drawn 9 Holes.					
28	0·106	2090	106·0	5	
	0·108	2290	108·0	4	
29	0·108	2180	106·0	3	29 and 29A are the same piece broken in two.
	0·110	2010	102·0	8	
29A	0·106	2190	111·0	4	
	0·108	2190	107·0	3	
Patented in 3-Gauge and drawn 8 Holes.					
30	0·107	2250	112·0	2	
	0·108	2160	105·0	4	

TABLE IX.—*The Effect of Hot Galvanising on Wire.*

Three full pieces of wire with the following compositions were taken :

(1) *Mild Steel Wire.*

	Per Cent.
Carbon	0·12
Silicon	0·04
Manganese	0·28
Sulphur	0·045
Phosphorus	0·031

(2) *Swedish* 0·60 *per cent. Carbon Steel Wire.*

	Per Cent.
Carbon	0·59
Silicon	0·27
Manganese	0·38
Sulphur	0·008
Phosphorus	0·029

(3) *Swedish* 0·80*per cent. Carbon Steel Wire.*

	Per Cent.
Carbon	0·81
Silicon	0·19
Manganese	0·32
Sulphur	trace
Phosphorus	0·033

A piece of each coil was galvanised at a temperature of 480° C. after receiving two, three, four, five, and six holes respectively, *i.e.* five pieces of wire from each set of the following S.W.G.'s were available—8½, 10, 11½. 13, and 14½.

The following mechanical tests were made on each piece before and after galvanising.

Tensile strength—lbs. per section and tons per square inch.
Torsions on 100 diameters.
Bends round 5 millimetres radius.
Elongation per cent.

SET No. 1.—*Mild Steel Wire.*

Before Galvanising.

S.W.G.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.	Bends.	Elongation per Cent.	Remarks.
		Lbs./Sect.	Tons per Sq. In.				
8½	0·152	1440	35·43	74	6	6·25	
10	0·127	1160	40·88	35	6	6·25	
11½	0·110	920	43·22	7	7	3·125	
13	0·092	760	50·9	4	8	2·344	
14½	0·075	520	52·4	5	9	2·344	
Mean .	...	**960**	**44·6**	**25**	**7**	**4**	
After Galvanising.							
8½	0·154	1400	33·56	83	5	14·06	
10	0·129	1080	36·9	16	5½	10·94	
11½	0·112	860	38·96	14	6	10·94	
13	0·094	650	41·83	12	8	12·5	
14½	0·077	460	44·12	12	10	12·5	
Mean .	...	**890**	**39·10**	**27**	**7**	**12**	
Loss or gain %	...	7·3	12	8	...	200	

TABLE IX.—(*continued*).

S.W.G.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.	Bends.	Elongation per Cent.	Remarks.
		Lbs./Sect.	Tons per Sq. In.				
			SET NO. 2.—*Swedish.* 0·60 *per cent. Carbon Steel Wire.*				
Before Galvanising.							
8½	0·152	3200	78·72	40	4	5·5	
10	0·128	2420	83·97	40	5	4·7	
11½	0·108	1860	90·63	42	7	4·7	
13	0·092	1440	96·70	45	9	3·1	
14½	0·077	10·40	99·72	43	11	3·1	
Mean .	...	**1992**	**89·95**	**42**	**7**	**4·22**	
After Galvanising.							
8½	0·154	3110	74·56	23	2	7·8	
10	0·130	2380	80·05	31	3	7·8	
11½	0·111	1790	82·56	31	4	7·8	
13	0·095	1370	86·26	30	5	7·8	
14½	0·079	1010	91·96	29	6	7·8	
Mean .	...	**1932**	**83·08**	**29**	**4**	**7·8**	
Loss or gain %	...	3	7·6	31	43	85	
			SET NO. 3.—*Swedish.* 0·80 *per cent. Carbon Steel Wire.*				
Before Galvanising.							
8½	0·152	3860	95·0	84	4	5·5	
10	0·127	3000	105·7	40	4	7·0	
11½	0·108	2280	111·0	43	6	6·25	
13	0·091	1750	120·0	40	7	6·25	
14½	0·076	1380	135·8	31	12	3·1	
Mean .	...	**2454**	**113·5**	**38**	**7**	**5·6**	
After Galvanising.							
8½	0·154	3700	88·7	13	2	7·8	
10	0·130	2800	94·2	11	2	6·25	
11½	0·1105	2200	101·5	18	4	6·25	
13	0·094	1650	106·0	15	4	6·25	
14½	0·078	1270	118·5	14	3	6·25	
Mean .	...	**2324**	**102·0**	**14**	**3**	**6·56**	
Loss or gain %	...	5·3	10	63	57	7·1	

TABLE X.—12-*Gauge Wire from Steel of the following composition :*

	Per Cent.
Carbon	0·73
Silicon	0·15
Manganese	0·67
Sulphur	0·041
Phosphorus	0·036

No.	Treatment.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.		Bends on 3 Diameters.	
			Lbs./Sect,	Tons per Sq. In.		Mean.		Mean.
1	As drawn	0·107	2520 2500	125	23, 25, 25	24	11, 11	11
2	30 seconds in zinc at 450° C. .	0·107	2220 2200	110	5, 18, 14	12	...	...
3	15 minutes in zinc at 450° C. .	0·107	1850 1860	92	8, 10, 12	10	...	...
4	1 minute in lead at 350° C. .	0·107	2480 2480	123	20, 20	20	9	9
5	1 ,, ,, 400 ,, .	0·107	2380	118	19, 18, 19	19	9½, 8, 8	8½
6	1 ,, ,, 450 ,, .	0·107	2200 2208	110	22, 9, 14	15	8, 7½, 6½	7
7	1 ,, ,, 500 ,, .	0·107	1930 1930	96	21, 9, 11	14	5½, 6, 5, 6, 6	6
8	1 ,, ,, 600 ,, .	0·107	1490 1488	74	32, 34	33	7, 7½, 11	8½

TABLE XI.—*Comparative Tests on the Influence of Carbon Content Before and After Galvanising.*

No.	Carbon per Cent.	Diameter. Inches.	Maximum Load.		Torsions on 100 Diameters.	
			Lbs./Sect.	Tons per Sq. In.		Mean.
1. Before . . .	0·44	0·032	270	151	40, 40	40
After . . .		0·032	230	129	32, 26, 23, 29	26
Loss . . .			15%			35%
2. Before . . .	0·44	0·037	295	127	37, 36	36·5
After . . .		0·037	250	104	34, 23, 26, 25	27
Loss . . .			15%			26%
3. Before . . .	0·85	0·037	320	134	43, 41	42
After . . .		0·037	270	113	31, 29, 25	28
Loss . . .			15·6%			33%

TABLE XII.—*Experiment* 18A. *Part* 1. *Tests on* $1\frac{1}{4}$ *inch Diameter Bars.*

No.	Treatment.	Diameter. Inches.	Maximum Load. Tons per Sq. In.	Elongation per Cent. on 2 Ins.	Reduction in Area per Cent.	Elastic limit. Tons per Sq. In.	Modulus of Elasticity. Tons per Sq. In.	Remarks.
1	$1\frac{1}{4}$-inch bar annealed at 900° C. and drawn to $\frac{13}{16}$ inch.	0·833	66	7·5	1	14·7	14,700	Broke in drawing, cuppy fracture. Tensile fracture short.
2	$1\frac{1}{4}$-inch bar patented at 900° C. and drawn to $\frac{3}{4}$-inch diameter.	0·758	75	10	27	12	12,500	Radial cracks in tensile fracture.
3	$\frac{3}{4}$-inch bar in 2, patented at 850° C. and drawn to 0·483 diameter.	0·483	81·5	12	39	24	12,000	,, ,,
4	,, ,,	0·483	76·4	11·5	40	Yield Point 63·2	...	Good fracture.
5	$\frac{3}{4}$-inch bar drawn to 0·575 inch without intermediate heat-treatment	0·575	84·1	9	27	46·8	...	Radial cracks.
6	,, ,, turned down for testing.	0·342	92·8	7	12	57·8	...	,, ,,

General Conclusions and Summary.

The results of the experiments of Part I. in conjunction with the evidence of microscopic analysis lead to the following conclusions:

1. The capacity to withstand cold-work is largely determined by the microstructure, and cannot be indicated entirely by the physical properties of the material; indeed material in a suitable condition for wire-drawing has poor physical properties.

2. In a properly drawn wire the crystalline grains are not broken up, but are elongated into fibres. Cold flow takes place within the grains and not by slip at the grain boundaries. There must, however, be movement at the boundaries accompanying the internal movement of the grain, and this intergranular movement will be greater or less according to the irregularity or uniformity of the internal flow. When this irregularity is great rupture will occur either at the boundary or through the grain and the material will be weakened..

3. When the grain is fully elongated into a fibre it cannot be subjected to further cold-work in the same direction without rupture, and when this occurs to any serious extent the material is over-drawn.

4. When an attempt is made to reduce the material too much at one pass the grains are broken. as in a tensile test, before the internal structure can adjust itself to the movement.

5. When the grains are very small, as in steels tempered after previous cold-work or drastic quenching, they have not the same capacity for elongation. Hence a fine-grained structure is not suitable for cold-working.

6. A coarse-grained structure has the greatest capacity to elongate into unbroken fibres, but, since such a structure is usually associated with over-heating and "ingotism," it is not always the most desirable.

7. The structure most suited to flow uniformly and to withstand the greatest reduction by cold-work, such as wire-drawing, is one in which the grains are large enough to elongate into fibres, and consists throughout of granular or cellular sorbite. The

statement that the capacity to withstand reduction by cold-work decreases with increase of carbon content is not universally true. In fine wires, where the flow is more or less uniform throughout the section, it is doubtless true. It is true also when the material is in the annealed condition, but in thick rods or bars the more uniform flow of the sorbitic condition permits of greater reduction by cold-work.

8. A structure consisting entirely of laminated pearlite, such as obtains in annealed eutectoid steels, is quite unsuitable for wire-drawing.

9. The high temperature employed for the heat-treatment operations in the manufacture of carbon steel wire is quite justified, and it would seem that 1000° C. is a suitable average temperature.

10. The structural effects of cold-work are not removed by annealing or tempering below the critical range, and such a process cannot replace "patenting."

11. While the ordinary tensile and torsion tests give a fairly reasonable measure of the quality of a wire, they might usefully be amplified by a rough measure of the percentage reduction in area. It has been shown that this begins to fall at approximately the same point as the torsion test.

12. Although cold-work reduces the ductility of the steel as indicated by the percentage elongation, it has still a capacity to withstand cold-work in a different plane, as shown by the increased percentage reduction in area and the resistance to fracture by twisting.

13. A careful analysis of the test results and curves in Part I. will indicate within what limits one may produce wire to a given specification in ordinary practice, and to what extent this might be improved by standardising the various processes, such as reduction per draught and heat-treatment in relation to the composition of the steel.

From the experiments on heat-treatment after cold-work in Part II. the following conclusions are summarised :

1. Any form of heat-treatment after cold-work below the recrystallising temperature (which lies between 500° and 600° C..

according to the class of steel) has, on the whole, a deleterious effect on the physical properties.

2. Although the elasticity and the percentage elongation are tests increased by such treatment, the bend and torsion tests show that the steel is in a brittle condition.

3. Time plays a very important part in this treatment, and such operations as hot-galvanising and tinning should be conducted as quickly as possible, so that the effects of heating are reduced to a minimum.

4. The low elastic limit in cold-worked steel indicates the presence of a mobile condition, and supports the amorphous cement theory of cold-work.

5. The recovery of elasticity accompanied by increased brittleness after heat-treatment and, to a slight extent, after ageing, supports the idea that the amorphous cement is unstable, passing from a viscous condition to a hard glassy or vitreous condition, and finally returning at a certain temperature to the crystalline condition.

6. The low elastic limit does not seriously affect the use of cold-worked material for many purposes, since the permanent set involved is negligible almost up to the breaking load, and without this slight mobility it is probable that the use of cold-worked material would be severely limited. On the other hand, the lack of elasticity may decrease its resistance to alternating stresses. It does not, however, necessarily follow that the fatigue limit coincides with the elastic limit, since the amorphous cement may be sufficiently mobile to yield to such stresses to a certain extent without rupture, and so prevent further slip in the cleavage planes.

It is for this reason that any research on the resistance of cold-worked material to alternating stresses will yield valuable information.

7. The structural effects of heat-treatment after cold-work are scarcely visible until recrystallisation commences. When this occurs the ferrite forms new grain boundaries, and the cementite collects in the form of nodules, which tend to coalesce.

This structure is typical in steels which have been heated below the critical range after cold-work. It constitutes a complete separation of the constituents of pearlite and sorbite.

In conclusion the author feels that many of the points raised in the work have been rather scantily treated, and it may seem that some of his conclusions are not supported by sufficient evidence. It was considered, however, that a broad survey of the whole field was required in order to show where closer investigation would be profitable.

BIBLIOGRAPHY.

Among the more important publications dealing with this side of the subject are :—

"The Heat Treatment of Wire, particularly Wire for Ropes." By J. D. Brunton, *Journal of the Iron and Steel Institute*, 1911, No. III.

"The Influence of Cold-Working and Annealing on the Properties of Iron and Steel." By P. Goerens. *Carnegie Scholarship Memoirs*, 1911, No. III.

"Some Aspects of Wire-Drawing." By P. Longmuir. *Journal of the Iron and Steel Institute*, 1912, No. II.

"Studies in the Cold Flow of Steel." By P. Longmuir. *Journal of the Iron and Steel Institute*, 1913, No. I.

DESCRIPTION OF PHOTOMICROGRAPHS.

Fig. 1.— × 250. Longitudinal section, 8-G wire, 0·44 C. Patented at 950° C. Cooled in lead at 500° C.

Fig. 2.— × 250. Longitudinal section, same wire drawn four passes to 13-G.

Fig. 3.— × 250. Longitudinal section, same wire drawn eleven passes to 22-G.

Fig. 4.— × 2500. Longitudinal section, 8-G wire, 0·44 C. Patented at 950° C. Cooled in air. Showing slight laminations in sorbite.

Fig. 5.— × 2500. Longitudinal section, 8-G wire, 0·44 C. Patented at 950° C. Cooled in lead at 500° C. Showing granular sorbite—best structure for drawing.

Fig. 6.— × 2500. Longitudinal section, 8-G wire, 0·85 C. Annealed at 900° C. Showing laminated pearlite—bad structure for drawing.

Fig. 7.— × 1500. Longitudinal section, drawn bar, 0·50 C. Showing slight laminations in sorbite after drawing.

Fig. 8.— × 3000. Longitudinal section, 0·75 C. Steel wire drawn two passes, showing structure partly sorbite and partly laminated pearlite. The rate of cooling here has been too slow, and irregular flow in drawing results from the presence of laminated pearlite.

Fig. 9.— × 2500. Longitudinal section, 0·44 C. Steel wire, showing effect of drawing on granular sorbite.

Fig. 10.— × 5000. Longitudinal section, 0·56 C. Steel wire over-drawn showing breakdown of sorbite and almost complete separation of the constituents by excessive cold-work.

Fig. 11.— × 4000. Longitudinal section, showing breakdown of sorbite assisted by free ferrite in drawing.

Fig. 12.— × 2500. Longitudinal section, same bar as in Fig. 7, after further drawing and at a higher power, showing more distinctly effect of cold-work on sorbite.

Fig. 13.— × 2500. Same section as Fig. 12. Heated to 600° C., showing complete " divorce " of sorbite after cold-work and annealing below the critical range.

PLATE V.

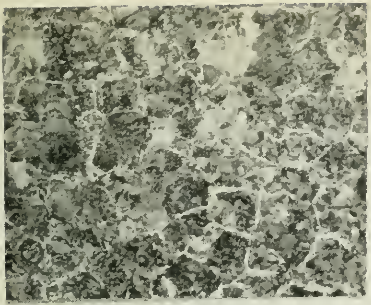
FIG. 1. × 250

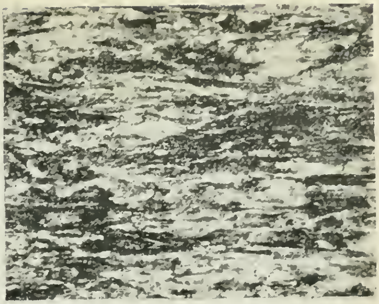
FIG. 2. × 250

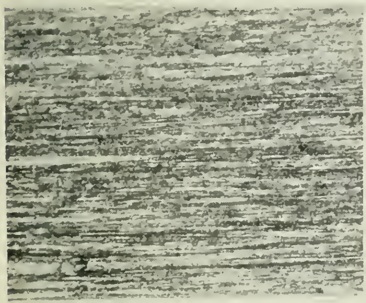
FIG. 3. × 250

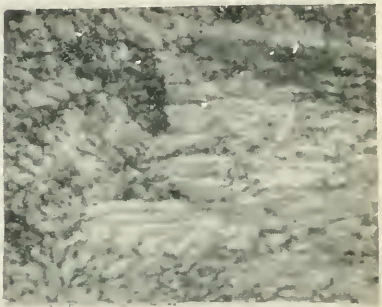
FIG. 4 × 2500

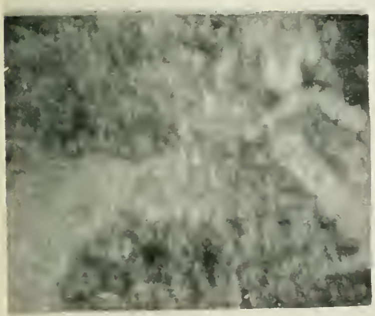
FIG. 5. × 2500

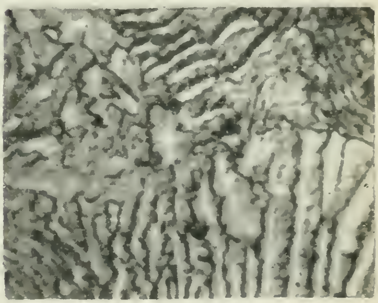
FIG. 6 × 2500

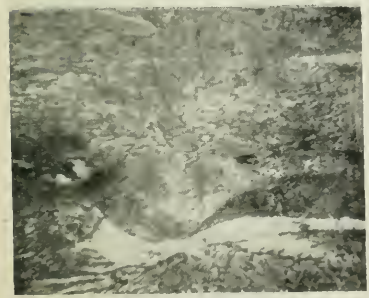
FIG. 7. × 1500

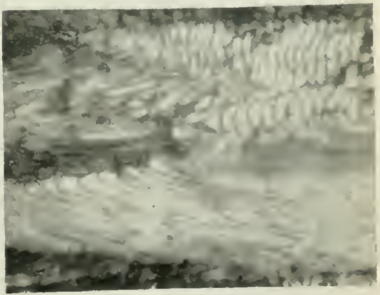
FIG. 8. × 3000

To face p. 128

PLATE VI.

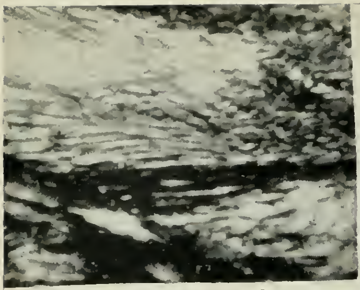

FIG. 9 ×2500

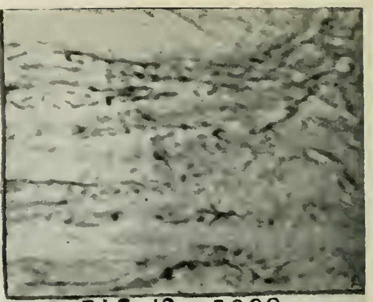

FIG. 10. ×5000

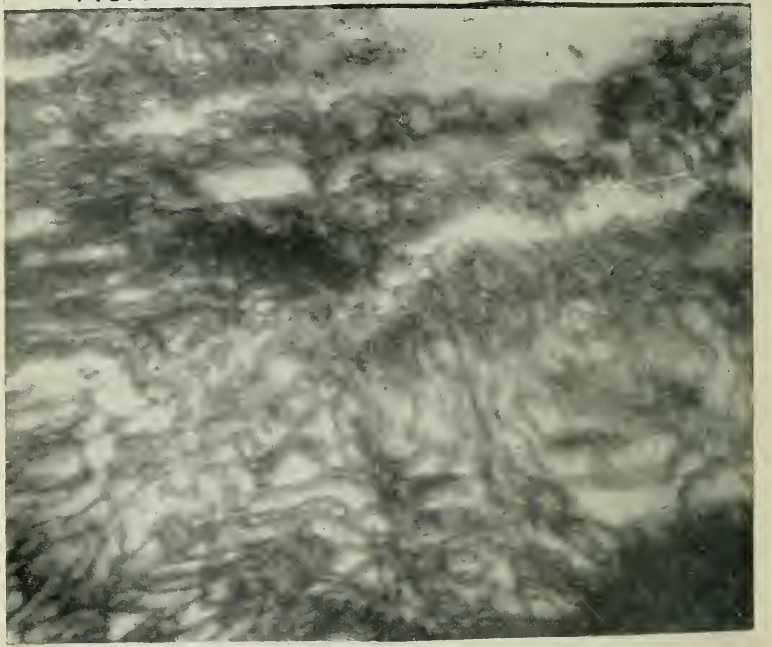

FIG. 11. ×4000

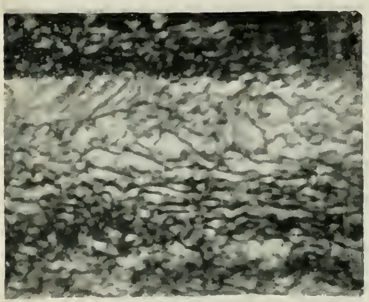

FIG. 12. ×2500

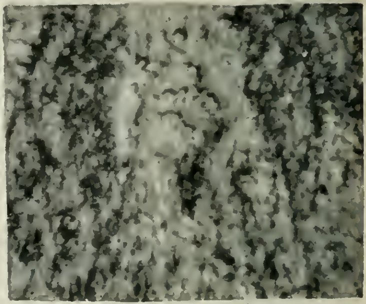

FIG. 13. ×2500

Iron and Steel Institute.

ALLOYS OF IRON AND URANIUM.[1]

BY E. P. POLUSHKIN (PARIS).

THE metal uranium has only recently begun to receive the consideration of the practical metallurgist, and up to the present very little systematic investigation of its influence and properties has been carried out.

The author has had the opportunity of studying the nature of ferro-uranium at the laboratory of one of the American chemical companies, and though his work was mainly devoted to research on uranium steels, nevertheless he presumes that some information, even if incomplete, concerning the comparatively recent product ferro-uranium may be of interest.

At the works in question uranium and vanadium are produced together as by-products after the extraction of radium from carnotite. The chemical composition of this mineral is: $(K_2 . Ca)O . 2UO_3 . V_2O_5 + 8H_2O$. Carnotite of the highest grade contains 50 per cent. U_3O_8, but the greater amount of ore is very low grade. Ore ranging from 1 per cent. to 1·5 per cent. of uranium oxide can be worked, though 2 per cent. ore is more desirable. After the extraction of radium, uranium is obtained as sodium uranate.

With a view to the practical application of uranium in making special alloys, ferro-uranium was produced. It was made in an electric furnace of the arc type, lined with a mixture of U_3O_8 and pitch, and having a water-cooled bottom. The charge consisted of uranium oxide, petroleum coke, and steel turnings. Fluorspar was added to the charge as a slag-forming material.

Several trials were made to reduce uranium with silicon, but ferro-uranium obtained by this method always contained a large proportion of silicon and other impurities; consequently it had no commercial value.

In the course of experimenting, many alloys with different contents of uranium and carbon were produced and tested. The alloys commonly used in making uranium steel contain 35 per cent. to 45 per cent. uranium, and 1 per cent. to 5 per cent. carbon. The highest proportion of uranium in all alloys obtained was 90 per cent., and the highest proportion of carbon was 8 per cent. The chemical analysis of alloys will be given later with a description of their microstructure.

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[1] Submitted to the Institute by the kindness of Col. N. T. Belaiew, C.B., on June 23, 1920.

Ferro-uranium is always well crystallised, especially in the case of alloys having U = 40 per cent. or higher, and C = 3·5 per cent. or higher, which are composed of well-formed black crystals. The superficial zone of the ingot is made up of small crystallites as usual in all alloys, but in the central zone large crystallites with sharp outlines are developed. Often in the centre flaky crystallites were found, evidently of the same origin and nature. The average chemical composition of the large crystallites and of the flaky crystallites was as follows:

	Uranium per Cent.	Carbon per Cent.	Iron (by Analysis) per Cent.	Silicon per Cent.	Vanadium per Cent.
Large crystallites .	48·21	5·36	42·80	1·80	1·51
Flakes . . .	50·75	5·46	39·8	1·56	1·38

Ferro-uranium is hard and pyrophoric. On crushing the ingot, sparking is noticeable. The pyrophoric property is increased the higher the proportion of uranium. Alloys reduced by silicon and having a high content of silicon (16 per cent. to 18 per cent.) with very low carbon are not pyrophoric, though they may contain as much as 40 per cent. uranium.

Determinations of specific gravity were made at room temperature, all samples being taken in equal weights of about 5 grammes. The specific gravity varied from 7·34 in the case of sample No. 31, containing 4·13 per cent. uranium and 90 per cent. of iron, up to about 12 in the case of samples Nos. 1 and 2, containing 90 per cent. uranium and 4·7 per cent. to 7·4 per cent. of iron.

Since some of the alloys decompose in water, pure alcohol was used in such cases. In alcohol the alloys do not show any trace of decomposition.

Moissan found the density of the uranium carbide C_3U_2 (C = 7·56 per cent.; U = 92·46 per cent.) equal to 11·28; the determination was made at 18° C. in benzene.

In general it is concluded that the density increases with an increase in uranium.

Determinations of the melting points were made in an electric furnace formed of a cylindrical graphite tube. The experiments were conducted under a stream of hydrogen conveyed to the tube without any special purification.

The samples were placed in an alundum boat and observations of the temperature were recorded by means of a Leeds-Northrup optical pyrometer.

In the first experiments the melting point was determined at the moment when marked changes occurred in the shape of the sample, namely, when the sharp outlines became rounded and the mass previously appearing above the boat almost immediately subsided, but later it was noticed that in heating ferro-uranium samples under these conditions a coating was formed which was not melted even when the metal itself had become fluid. This solid formation retained its outlines unbroken at a much higher temperature than was necessary for the melting of the metal. Samples taken from the furnace showed the molten metal lying side by side with the shell from which the metal had escaped.

This formation is apparently an oxide of uranium, and its origin can be fully explained by the fact that the walls of the graphite tube are not dense enough to prevent diffusion of the air from the outside. This method was therefore abandoned and a new one was tried.

Four or five samples were placed in the boat in a certain order, being separated one from the other by finely powdered alumina. The furnace was then heated under the stream of hydrogen up to a certain definite range of temperature, at which it was maintained from twenty to thirty minutes. After cooling under the stream of hydrogen, the samples were removed and broken up. The structure showed which samples were melted and which were not. For the next experiment fresh samples from those alloys which had not melted in the previous experiment were now subjected to heating at a lower temperature.

Repeated experiments finally determined the temperature at which no melting took place.

The lower limit being settled, further experiments were made to discover the upper in a similar way. By this method it was possible to determine the melting point within definite limits, but the formation of a coating on the samples could not be avoided.

Table I. shows the melting points of four alloys.

TABLE I.

Alloy No.	Uranium per Cent.	Carbon per Cent.	Iron (by Analysis) per Cent.	Silicon per Cent.	Vanadium per Cent.	Aluminium per Cent.	Range of Temperatures in which the Melting Point is Located.		Number of Determinations.
							Upper Limit Degrees C.	Lower Limit Degrees C.	
10	28·7	0·34	66·81	1·44	0·53	...	1660	1540	3
35	41·6	4·57	46·88	3·55	1·76	...	1785	1660	2
21	47·5	2·29	47·40	2·59	1·66	...	1710	1660	6
3	55·2	0·98	41·9	1.11	0·71	...	1785	1660	3
19	85·2	7·42	2·41	1·45	2·07	0·08	Disintegrated into powder at 1000° C.		

The many difficulties due to the very high temperatures involved and the rapid oxidation of uranium indicated that these determinations would be better made in a vacuum furnace.

Decomposition of Ferro-Uranium by Water.—Moissan found that uranium carbide having a composition of U_2C_3 is decomposed by cold water. The author's experiments show that several ferro-uranium alloys are apt to be decomposed by water. For the purpose of thoroughly investigating this phenomenon, alloys of different content of uranium were subjected to immersion in water and kept there for at least one day. The decay began usually very soon after immersion. It consisted in the separation of the particles from the alloy, accompanied by evolution of gas rising in the form of bubbles, carrying the finest particles to the surface of the water. The odour of this gas resembled that of acetylene, and when ignited it burned with a blue flame.

Tables II. and III. show the principal ferro-uranium alloys decomposable and non-decomposable by water.

TABLE II.—*Alloys Decomposable by Water.*

Alloy No.	Uranium per Cent.	Carbon per Cent.	Iron (by Analysis) per Cent.	Silicon per Cent.	Vanadium per Cent.	Remarks.
6	39·9	1·08	48·69	3·99	3·47	Rapidly.
1	90·0	2·33	3·42	1·13	1·84	,,
2	90·1	1·22	...	0·16	1·12	,,
19	85·2	7·42	2·41	1·45	2·07	,,
41	47·0	1·19	...	...	...	,,
42	41·4	1·22	...	...	...	Slowly
43	47·2	2·39	...	...	...	,,
44	41·5	1·53	...	2·47	1·97	Mn = 3·40 Slowly.
45	50·1	1·34	47·58	1·61	0·15	Slowly.
7	41·6	0·74	53·8	1·90	0·75	Partially.
46	39·40	0·92	55·9	1·89	0·63	,,
39	49·8	1·15	42·40	2·64	3·38	,,

TABLE III.—*Alloys Non-Decomposable by Water.*

Alloy No.	Uranium per Cent.	Carbon per Cent.	Iron (by Analysis) per Cent.	Silicon per Cent.	Vanadium per Cent.	Remarks.
33	45·3	1·13	34	19·4	...	
32	20·2	2·40	...	3·84	...	
23	44·5	5·03	46·10	2·24	1·38	Al = 0·05
47	37·8	4·12	...	2·59	1·25	
48	30·5	1·20	...	3·94	1·87	
12	15·8	0·52	73·74	3·53	4·58	
49	35·7	3·04	58·1	1·34	0·46	
3	55·2	0·98	41·9	1·11	0·71	
50	0·68	0·07	98·77	0·07	0·09	
51	40·85	1·49	55·78	1·25	0·32	
52	47·2	2·76	...	9·82	5·79	
53	27·6	1·34	...	6·06	3·26	
54	40·4	0·71	55·1	1·72	0·68	
35	41·6	4·57	46·88	3·55	1·76	
11	20·5	1·10	76·85	0·87	0·36	

Comparing these tables the following conclusions may be drawn:

(*a*) Only those alloys containing 40 per cent. or more of uranium are capable of being decomposed by water.

(*b*) In all decomposable alloys of the series containing from 40 per cent. to 55 per cent. of uranium the carbon content is comparatively low. Each alloy of the same series whose content of carbon is 3 per cent. or over is non-decomposable.

(*c*) On the other hand, alloys of the same series having a very low proportion of carbon—0·70 per cent. or lower—are also non-decomposable.

(*d*) Alloys of such a high content of uranium as 85 per cent. to 90 per cent. are decomposable, though the carbon in them may vary from 1·2 per cent. to 7·4 per cent.

(*e*) Apparently vanadium and silicon have no influence upon decomposition, except when the proportion of silicon is extremely high, as in the alloy of No. 33 ; in this case silicon has apparently a preventative action upon decomposition.

The cause of the decomposition remains yet to be discovered. It is not improbable that a part of the uranium present in a decomposable alloy is there in a special form—for example, in the form of U*x*, which dissolves in water ; if this be so, it may induce decomposition. Or, as Moissan asserts, the presence of the hydrogen in the gaseous mixture produced during decomposition may be due to the secondary action of hydrated uranium oxide, which must be a powerful reducer. Peligot demonstrated formerly that anhydrous uranium protoxide has a great avidity for oxygen, and that an oxide of uranium existed which possessed the property of decomposing water.

Radio-activity of Ferro-Uranium.—Uranium being a radio-active element, ferro-uranium also possesses radio-activity. This property has been utilised at the laboratory of the works for the purpose of determining roughly the proportion of uranium in an alloy. In order to do this the Curie electroscope was employed. The data obtained are not exact and could be only used for the purpose of preliminary comparison.

The radio-active properties of ferro-uranium may also be studied on a photographic plate. If a polished sample be put on the emulsion of the plate and left there for several days, or even several weeks, it leaves an impression on the plate which after the usual development gives a radiograph of the structure. This method permits the recognition of those constituents of uranium alloys which contain uranium.

Solubility of Ferro-Uranium in Steel.—Steel was made in the ordinary way in an electric furnace, and ferro-uranium was added either in the furnace before tapping or in the ladle. In both cases the chemical analysis, physical tests, and microscopical examination revealed no difference in the properties or in the structure of steel, the distribution of uranium in the steel being invariably uniform. Drillings taken from the top and bottom of ingots gave nearly the same amount of uranium. The real difference existed, however, in recovery. When uranium was added in the furnace, the greater portion was burnt out and recovery was low; while, if addition were made in the ladle, the recovery often reached 70 per cent. to 75 per cent. Generally speaking, recovery was irregular, sometimes being 50 per cent. or even lower.

Two special experiments were carried out for the purpose of ascertaining solubility of uranium in steel. The steel made in the electric furnace was poured into the ladle, and thence into eight graphite crucibles (in each experiment), previously heated red-hot. Ferro-uranium was added to each crucible in pieces of the size of a pea just before filling. Ingots of about 30 lbs. weight were annealed after cooling and were then sawn in half, drillings being taken for chemical analysis from cross sections from the top and bottom of the ingot. Ten ingots gave recovery of 70 per cent. or over, two ingots 65 per cent. to 64 per cent., and four ingots 53 per cent. to 37 per cent. The average analysis of steel obtained in the first experiment was:

$$C = 0{\cdot}85,\ U = 0{\cdot}79,\ Si = 0{\cdot}65,\ P = 0{\cdot}04,\ S = 0{\cdot}02;$$

in the second experiment:

$$C = 0{\cdot}65,\ U = 0{\cdot}75,\ Si = 0{\cdot}52,\ P = 0{\cdot}03,\ S = 0{\cdot}01.$$

The difference in uranium content at the bottom and at the top of the ingots was negligible.

The samples of ferro-uranium added to the steel had: uranium from 30 per cent. to 50 per cent., carbon from 0·60 per cent. to 4 per cent., silicon from 2·5 per cent. to 6 per cent., vanadium from 1·25 per cent. to 3·25 per cent.

Alloys with uranium content between 30 per cent. and 40 per cent. showed the best recovery. The proportion of carbon appears to have no influence upon the results.

The longitudinal sections of the first eight ingots were etched with picric acid and examined. Each ingot had one large blowhole in the centre, which evidently was developed under the pressure of gas. White spots were found surrounding these holes, wherein the carbon was burnt out entirely. This is evidently due to the action of the air penetrating the metal through the cavity. The balance of metal seemed to be sound and dense. The microstructure showed a uniform distribution of uranium in the steel.

Thus, the results of these experiments, as well as the regular practice in making experimental steel at the works, showed that ferro-uranium is easily dissolved in the liquid steel.

The question then arises: In what form is uranium present in steel? All the observations of different samples under the microscope invariably demonstrated the presence of uranium oxide. While one part of the uranium was in the form of carbide, the other part was in the form of oxide, the latter being invariably found in all steels, though their composition varied widely. Even steels with a high proportion of silicon, manganese, chromium, and nickel had a considerable amount of uranium oxide. Evidently a portion of ferro-uranium added to the steel was oxidised during the process of its dissolution, but owing to the oxide of uranium being heavy, it could not rise to the top of the ingot and remained within the metal.

Thus, to find the actually useful proportion of the whole addition of ferro-uranium, it would be necessary first to determine by analysis the amount of uranium oxide present.

MICROSTRUCTURE.

The ferro-uranium alloys investigated were very complex, being composed of five components: iron, uranium, carbon, vanadium, and silicon. The proportion of other elements present was so small that they can be considered as impurities. The approximate chemical composition of these alloys has not yet been determined, and the only method used for identifying the different constituents of the alloys was by examination under the microscope after etching them with suitable reagents, and secondly, by observing the changes in the microstructure of the whole series of alloys produced by increasing or decreasing one or two components.

All alloys were submitted to similar treatment; they were etched with picric acid and then immersed in a bath of tin for heat-tinting (Stead method). For the purpose of separating some of the constituents one from the other, various etching reagents were in many cases also applied.

The microstructure of at least fifty different uranium alloys not including uranium steel were microscopically studied. Table IV. shows some of the alloys hitherto examined, together with their analysis and their structural composition. The constituents are enumerated in the order corresponding with their proportions in an alloy (as far as can be ascertained under the microscope). The new constituents are designated by the first letters of the Greek alphabet, and their hypothetical chemical compositions are enclosed in brackets ( ).

The chemical composition given in the following table was nearly always calculated as an average of several determinations.

The nature of every constituent is shortly described below.

Group of Carbides.

1. Uranium carbide alpha. Hypothetical formula UC. Etching with picric acid causes it to appear pale grey, the dark colour being increased with the prolonged action of the reagent.

After heat-tinting it assumes different delicate colours such as: bluish, dark bluish, greenish, and pale violet, each grain taking an individual coloration. This coloration is retained after slight polishing.

Reagents in which it will dissolve: $HgCl_2$,[1] HCl (1·18), sodium picrate, HF. Strong acids HNO_3 and H_2SO_4 will dissolve it more slowly than strong HCl. It is easily dissolved by aqua regia, which reveals its crystalline structure.

The carbide frequently appears in well-formed crystals. In some alloys it is found with ferrite as a fine mixture similar to eutectic which has been designated eutectic [alpha + Fe]. Fig. 1 represents grey crystals of alpha as well as [alpha + Fe]. Very often small formations of alpha contain crystals of the

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[1] $HgCl_2$ was used in all these experiments in a saturated solution with alcohol.

Table IV.

Alloy No.	Uranium per Cent.	Carbon per Cent.	Iron (by Analysis) per Cent.	Silicon per Cent.	Vanadium per Cent.	Structural Composition.
Series I.—Uranium Carbides.						
1	90·0	4·10 2·05 2·62	3·42	1·13	1·84	Carbide alpha (UC) + U oxide (U_3O_8) + FeSi + carbide theta (V_2C).
2	90·1	2·34 1·19 1·24	...	0·16	1·12	Do. Do.
19	85·2	7·42[1]	2·41	1·45	2·07	Carbide U_2C_3 + FeSi + theta (V_2C).
Series II.—Alloys with a Small Proportion of Carbon.						
3	54·5	0·90	41·8	1·11	0·71	Beta (Fe_6U) + [gamma (U) + Fe][2] + Fe + [alpha (UC) + Fe] + carbide delta.
5	39·7	0·63	52·0	2·93	2·95	Beta (Fe_6U) + [gamma (U) + Fe] + gamma (U) + theta (V_2C) + carbide iota (Fe_3C . U_2C_3) + alpha (UC).
6	40·4	1·1	48·7	3·9	3·5	Beta (Fe_6U) + alpha (UC) + FeSi + theta (V_2C).
7	39·4	0·75	53·8	1·89	0·75	Beta (Fe_6U) + [gamma (U) + Fe] + alpha (UC) + carbide delta.
11	20·5	1·10	76·85	0·87	0·36	Fe + [alpha (UC) + Fe] + beta (Fe_6U).
12	17·1	0·53	73·7	3·50	4·60	Fe + beta (Fe_6U) + theta (V_2C) + alpha (UC).
16	7·05	0·46	...	0·71	0·15	Fe + pearlite + alpha (UC) + beta (Fe_6U).
17	2·49	0·28	...	0·41	0·06	Do. Do.
18	1·21	0·21	...	...	...	Do. Do.
Series III.—Alloys having Carbon = 2·3 per Cent. or Higher.						
22	45·6	3·50	47·40	1·85	1·66	Alpha (UC) + iota (Fe_3C . U_2C_3) + [alpha (UC) + Fe] + beta (Fe_6U) + Fe.
23	44·5	5·0	46·1	2·2	1·3	Iota (Fe_3C . U_2C_3) + pearlite + FeSi + theta (V_2C) + graphite.
25	40·6	2·31	50·8	2·22	2·61	Alpha (UC) + [alpha (UC) + Fe] + iota (Fe_3C . U_2C_2) + beta (Fe_6U) + Fe.
28	16·5	3·42	75·90	4·0	1·61	[Beta (Fe_6U) + Fe_3C] + Fe_3C + pearlite + theta (V_2C) + alpha (UC).
31	4·1	3·0	89·6	1·1	1·4	[Fe_3C + pearlite] + pearlite + Fe_3C + beta (Fe_6U) + theta (V_2C) + alpha (UC).

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[1] 7·42 per cent. includes 0·58 per cent. graphite.

[2] Aggregates similar to eutectic are enclosed in square brackets [ ].

other constituent beta, which remained white after heat tinting (Fig. 2).

Alloys No. 1 and 2 containing 90 per cent. of uranium are composed mainly of alpha ; it is likewise well developed in Nos. 11, 21, 25.

The chemical composition of alpha was determined by the consideration of the alloy No. 11, this alloy being composed only of two constituents—viz. ferrite and carbide alpha, the latter alone carrying all the uranium and carbon present in this alloy. The formula UC requires 1·03 per cent. of carbon to combine with 20·5 per cent. of uranium in No. 11, according to the proportion :

$$238{\cdot}2 : 12 = 20{\cdot}5 : x.$$

Analysis attributed 1·10 per cent. to the carbon in this alloy. This insignificant difference of 0·07 per cent. may be due not only to inaccuracy of analysis, but also to the fact that a small portion of carbon must be combined with vanadium.

Carbide alpha is present in uranium steel ; it does not pass into a solid solution with iron even at 1200–1250° C., as the experiments with uranium steel showed.

2. Uranium carbide U_2C_3. This carbide was only found in one alloy, No. 19, the alloy being almost entirely composed of it. After heat tinting it becomes first dark brown and afterwards dark bluish grey. It is more soluble by aqua regia than carbide iota. U_2C_3 forms plate crystals. Water decomposes it.

3. Iron-uranium carbide iota. (Alloy No. 5.) Hypothetical formula $Fe_3C \,.\, U_2C_3$. After etching with picric acid it appears light grey, in strong relief, usually in the form of elongated crystals. Heat-tinting gives dark colouring in blue, green, or violet, but these colours are rapidly transformed into bluish-grey. The coloration is retained after slight polishing. This carbide strongly resists etching even with aqua regia, which affects it very slowly. Apparently HCl (1·18 per cent.), HNO_3 (10 per cent. in alcohol), and $HgCl_2$ do not affect it. Sodium picrate imparts brown colouring. HF colours the carbide with light colours and then causes etching pits to appear. It is strongly radio-active, is harder than the other uranium constituents (it scratches glass), and is not decomposable by

water. It nearly always appears in the form of very well formed plate crystals (Fig. 3) which under favourable conditions are developed into large black flakes, often found in the central cavity of ingots.

In the flakes uranium averages 50·75 per cent.; iron 39·8 per cent.; carbon 5·46 per cent.; silicon 1·56 per cent.; and vanadium 1·38 per cent.; 5·1 per cent. of carbon is required by the formula $Fe_3C \,.\, U_2C_3$ to combine with 50·75 per cent. uranium, according to the proportion :

$$50{\cdot}75 : C = 476{\cdot}4 : 48.$$

The difference, 0·35 per cent of carbon, is combined partly with vanadium in V_2C and partly by Fe_3C in pearlite.

Further the same formula requires Fe :

$$Fe : 50{\cdot}75 = 168 : 476{\cdot}4 ;\ Fe = 18{\cdot}3 \text{ per cent.}$$

The balance of iron, 21·5 per cent., is combined with carbon in cementite of pearlite and with silicon in FeSi :

1·38 per cent. V in V_2C requires 0·16 per cent. of carbon.
1·56 per cent. Si in FeSi ,, 3·12 per cent. of iron.

The balance of Fe = 17·38 being in pearlite requires 0·15 per cent. carbon.

The approximate chemical composition of the flakes will be :

	Per Cent.	
$Fe_3C \,.\, U_2C_3$	74·15	
V_2C	1·54	
FeSi	4·68	
Fe_3C in pearlite	2·25	pearlite.
Fe ,,	15·28	
	97·90	

This carbide is among the first to separate from a solution of iron and carbon. This is well demonstrated by the good appearance of iota crystals as well as by the commanding position they take among the other constituents.

Iota ranks as the principal constituent in alloys having U = 33 per cent. or higher, and carbon 4·0 per cent. or higher. It has also been found, however, in alloys with very low proportions of carbon. Carbide iota does not form a eutectic with iron.

4. Double uranium carbide delta is found in a very limited amount and only in separate grains. The delta crystals possess duplicated edges, having within a very hard substance surrounded by a softer and more greyish crystalline envelope (Fig. 4). Delta is rather rare and does not play any important rôle in the structure of ferro-uranium alloys. It is present mainly in alloys with a small proportion of carbon.

5. Vanadium carbide V_2C (theta). This appears as white brilliant grains, very hard, usually irregular in form and partly removed by polishing (see dark spots with white centres in Fig. 5).

Heat-tinting does not colour it at all. A special sample of vanadium carbide submitted to heat-tinting assumed a slight yellow colour, but only after long and repeated heatings.

Picric acid, sodium picrate, $HgCl_2$, HCl, H_2SO_4 (10 per cent. in water), HNO_3 (10 per cent.), and strong (1·18 per cent.) tincture of iodine do not dissolve or colour it. HF dissolves it slowly.

Its chemical composition was determined by consideration of the structure of the alloy No 12. This alloy has 4·60 per cent. vanadium and 0·53 per cent. carbon, the balance being iron, uranium, and silicon. None of the above-mentioned uranium carbides was found in the alloy (except a very insignificant amount of alpha), uranium (17·1 per cent.) being entirely combined here with iron. This alloy demonstrates that vanadium has more affinity for carbon than uranium.

Other Constituents.

6. Compound of iron and uranium (beta). Hypothetical composition Fe_6U. When carbon is present in an alloy in a small proportion, or when it is entirely combined with vanadium or iron, the uranium enters into a special compound Fe_6U with iron, if present in considerable proportion.

After etching with picric acid beta is white or slightly grey, lying in relief. After heat-tinting it becomes yellowish brown, though lighter than ferrite. It is harder than ferrite, but softer than carbides theta and iota.

Aqua regia dissolves and colours beta light violet ; sodium picrate colours it yellow, green and other colours. $HgCl_2$ and tincture of iodine apparently do not dissolve it.

The chemical composition of beta was determined by consideration of the structure of the alloy No. 6 composed mostly of beta. In this alloy carbon is combined with vanadium (V_2C) and with uranium (UC); 3·5 per cent. vanadium in V_2C requires 0·41 per cent. of carbon. The balance of carbon 0·60 per cent. in UC requires 11·9 per cent. of uranium; 3·9 per cent. silicon in FeSi requires 7·8 per cent. iron. The balance of iron 40·9 per cent. in Fe_6U would require 29 per cent. uranium, and then the total of uranium in the alloy would be 40·9 per cent. As a matter of fact the analysis gave U = 40·4 per cent.; therefore the difference is only 0·5 per cent.

7. Gamma—metallic uranium. In those alloys, wherein carbon is entirely combined with vanadium and uranium, iron is combined with uranium and silicon, and where an excess of uranium still exists, uranium may be present in a pure state. Take, for instance, alloy No. 3: 0·71 per cent. vanadium in V_2C requires 0·08 per cent. carbon. The balance of carbon 0·82 per cent. in UC requires 16·4 per cent. uranium; 1·11 per cent. silicon in FeSi requires 2·22 per cent. iron. The balance of U = 38·1 per cent. The balance of iron 39·58 per cent. in Fe_6U would require 28 per cent. uranium, that is, 10 per cent. less than is present in this alloy. A certain part of the iron exists, however, in the form of ferrite; so a still greater part of uranium must be present in a pure state (Fig. 6). Gamma is softer than alpha and is not always smooth. Etching with picric acid turns it grey.

8. Ferrite (Fe) has the ordinary appearance. The reagents act upon it very strongly. Etching with tincture of iodine reveals the cubic structure of ferrite.

9. Pearlite is not found in alloys with a low carbon percentage, except in the case of uranium steels. Medium and high carbon alloys, however, often contain it, but not always. Pearlite containing uranium seems darker than the normal pearlite.

10. Silicide FeSi. Brittle white constituent usually full of cracks. It pertains to those alloys possessing a high proportion of silicon and a small amount of free ferrite. After heat-tinting it does not assume any colouring. Picric acid and $HgCl_2$ do not act upon it. HF colours it brown, forms the cracks and dissolves it rapidly.

11. Graphite. Primary graphite has a more regular shape. It appears sometimes in the form of several rays from one centre. Secondary graphite has no regular shape.

12. Uranium oxide U_3O_8. Dark grey, dark bluish constituent which is not changed after heat-tinting. It may be found in all alloys, including uranium steels, wherein it is embedded as small separated inclusions. In alloys with a high proportion of uranium and a small or moderate content of carbon it abounds and may occupy a considerable part of their polished surface. Aqua regia dissolves it, producing dark etching pits. HCl (strong) produces linear etching pits. It is dissolved also in HF, H_2SO_4, and HNO_3.

Description of the Structure of the Separate Alloys.

Series I.—In his research the author took three alloys with the highest uranium content—Nos. 1, 2, and 19. The two former have the same microstructure; their polished surface revealed three distinctive constituents without etching. The principal one, covering the greater part of the polished surface, is of a slightly greyish colour (Fig. 7) and forms grains with rounded outlines. The next one is quite white and smooth, its amount being small in comparison with the first. The third one is dark grey to slightly bluish, and rough; it is irregularly distributed among its companions. Some parts of the samples Nos. 1 and 2 have the third constituent in abundance and some are almost free from it.

Etching with common diluted acids shows that the first constituent gradually dissolves and the others remain unchanged. Deep etching with aqua regia clearly demonstrates the crystalline nature of the principal constituent.

The most interesting phenomenon is revealed when the polished samples Nos. 1 and 2 are submitted to heat-tinting in a bath of tin. The samples must be previously etched by picric acid or by some other mild reagent for the purpose of removing the amorphous layer of metal formed by polishing. Afterwards they must be placed in liquid tin leaving the polished surface exposed to the air. When this surface assumes a distinctive yellow colour the samples are removed and cooled. The grains of the principal constituent then appear under the microscope tinted in beautiful soft colours—bluish, dark bluish, greenish, violet—each grain having an individual coloration. The colours are not very bright, but very soft and slightly greyish. The red, the orange, and the yellow are not present. Meanwhile the other two constituents are not changed, so the polished surface resembles a mosaic of faintly coloured enamels of different shades with portions of a white setting showing between. Fig. 8 is only a monochromatic photograph and can give no idea of this picture. The more likely cause of different coloration of grains is found in their different crystallographic orientation. If heating is carried on longer, all grains change to bluish grey.

The investigations showed that the principal constituent is uranium carbide alpha (UC); the white constituent is composed partly of silicide and partly of vanadium carbide (V_2C), and the dark grey constituent is uranium oxide (U_3O_8).

The alloy No. 19 has an entirely different structure. Etching reveals that the alloy is composed of white plate crystals. The proportion of carbon is 7·42 per cent. including 0·58 per cent. graphite, *i.e.* carbon combined is equal 6·87 per cent. Vanadium carbide contains 0·24 per cent. of carbon. The balance of carbon 6·60 per cent. must be combined with uranium. According to the formula U_2C_3, 85·2 per cent. uranium would require 6·44 per cent. carbon; the difference is only 0·16 per cent., which may be easily attributed to the inaccuracy of the analysis. This carbide is identical with that found by Moissan. It is also decomposed by water.

Series II.—In these series have been classified the alloys having a low percentage of carbon (not higher than 1·13 per cent.). This element plays the most important rôle in the structure.

In alloys Nos. 3, 5, 6, and 7 the principal constituent is beta, Fe_6U; in all others, ferrite. Nearly all the members of the first group contain metallic uranium (gamma), this being present in considerable proportions in alloy No. 3. It forms a eutectic with iron. The occurrence of gamma in these two alloys can be easily understood, taking into consideration their proximate compositions.

Alloys 5 and 6 are not dense, seeing they contain an increased proportion of FeSi and V_2C which, being brittle, were partially removed by polishing and cavities were left. Owing to the greater amount of carbon in No. 6, the proportion of free uranium in the latter alloy is much less—almost negligible ; but the proportion of UC is increased.

Crystals of beta in No. 5 are well formed, while in No. 6 almost the entire mass of the alloy is composed of beta, and beta has no definite outlines. Alloy 7 is similar to Nos. 5 and 6, except that it is dense.

No pearlite is discovered in any of the alloys belonging to this first group (Fig. 9).

The second group has ferrite as the predominating constituent. These alloys may be classified into two divisions :

(*a*) Non-pearlitic alloys (Nos. 11–12),
(*b*) Pearlitic steels,

—the main constituents in the first division being ferrite and Fe_6U, and in the second ferrite and pearlite. The occurrence of pearlite in steels is due to the fact that carbon is not combined here with vanadium or with a large amount of uranium, as is the case with the first division of alloys.

Alloy No. 11 has only ferrite and carbide alpha. The only constituent which could contain uranium or carbon is alpha, consequently the chemical composition of carbide alpha can be calculated, which has already been done in the description given of this carbide. Beta is found here only in very insignificant proportion, in the form of minute separate crystals in the midst of the carbides.

In alloy No. 12 three constituents have been found : silicoferrite, beta, and vanadium carbide (V_2C) ; the rare and minute inclusions of alpha need not be reckoned. From this alloy the chemical composition of vanadium carbide, the only carbon bearer, has been determined (see description of V_2C) ; 17·1 per cent. uranium in Fe_6U requires 24·1 per cent. of iron, so the balance of iron is 49 6 per cent. Thus the approximate structural composition of No. 12 will be :

	Per Cent.
Ferrite (including FeSi) . . .	53·1
Fe_6U	41·2
V_2C	5·04
	99·34

Steels 16, 17 and 18 have pearlitic structure with hirsute inclusions of uranium carbide alpha. Alpha contains also a certain amount of Fe_6U, as is shown in Fig. 2. The carbide alpha (UC) does not resolve itself into a solid solution with iron, and remains independent (Fig. 10) even if quenched in water at a temperature as high as 1200° to 1250° C. Fe_6U also remains unaffected by the solution. Quenching was powerless to diminish ever so little the amount of uranium carbide in any of the steels. Meanwhile pearlite disappeared and the hardness of the samples increased. This may be considered as a proof that pearlite rather contains a simple cementite than a double carbide of iron and uranium.

Series III.—It may be seen from Table IV. that alloys having uranium in the proportion of 33 per cent. or higher and carbon not less than 4·3 per cent. contain double carbide $Fe_3C \cdot U_2C_3$ which must be considered as a distinctive constituent of their structure (first group).

Alloys Nos. 22 and 25 include much less carbon and reckon simple uranium carbide alpha as their main constituent (second group).

Finally the other alloys of the same series (Nos. 28 and 31) may be characterised as possessing cementite as their distinctive constituent (third group).

The more distinguishing structure of the first group of alloys has been already shown in Fig. 3. For the purpose of differentiating the uranium constituents from the others, the radiographic method was applied. Alloy No. 23 was first studied by this method, which was afterwards applied to many other alloys.

The polished surface of a sample having previously been etched with picric acid was placed upon the emulsion of the photographic plate and left there for at least several days and often for several weeks. The time of the exposure depends upon the proportion of uranium in alloy; the larger the proportion the less the exposure. It is rather to be recommended that the sample be fixed slightly above the surface of the plate to avoid damage to the plate by scratching. The development and fixing of the plate were as usual. A figure appeared on the plate in which the radio-active constituents were seen to have left traces of their presence in the form of dark lines or spots (Fig. 11). This fine micrograph was observed further under the microscope, the plate being placed on the microscope objective with its emulsion side downward. Those portions in the structure which were found more suitable for comparison were photographed under slight magnification (magnification 20–25 diameters was used). Then the polished surface of the sample used for radiography was observed likewise under the same magnification, and the identical portions of the structure were found and compared with their image on the plate. Plate VIII. shows two photographs (Figs. 12 and 13) of the alloy No. 23—one taken directly from the sample, the other from the radiograph, both magnified to the same degree (× 24 diameters). Attention is directed to the large right-angled triangle (its position is reversed from left to right in the radiograph). This triangle has three main lines parallel to its base, two lines parallel to one of the sides as well as several oblique lines. Thus carbide iota exposed along all these lines showed itself strongly radioactive—that is, containing a considerable amount of uranium.

Meanwhile the white rounded masses inside this triangle left no impressions; consequently they do not contain uranium, and must represent silicide and vanadium carbide (Fig. 14). This micrograph shows also pearlite associated with fine needles of carbide iota.

The structural composition of alloy No. 23 may be quite satisfactorily interpreted if we accept the formula of carbide iota as being $Fe_3C \, . \, U_2C_3$: 44·5 per cent. of the uranium in $Fe_3C \, . \, U_2C_3$ requires 4·5 per cent. carbon and 16 per cent. iron. The balance of carbon, 0·5 per cent., is represented by pearlite, V_2C, and graphite.

Judging by the amount of pearlite present in the alloy, it must be assumed that approximately 0·25 per cent. of carbon exists in pearlite; 0·25 per cent. carbon gives 3·75 per cent. of cementite, or 30 per cent. of pearlite. The amount of ferrite in pearlite is: 30 per cent. minus 3·75 per cent. = 26·25 per cent.: the balance of ferrite is: 46·1 per cent. minus 16 per cent. minus 26·25 per cent. = 3·85 per cent.: 3·85 per cent. iron in ferrosilicon needs 1·92 per cent. of silicon—in fact we have in this alloy 2·2 per cent. of silicon, this being near the amount required:

1·3 per cent. vanadium in V_2C demands 0·15 per cent. carbon; the balance of carbon is 0·10 per cent. in form of graphite.

Thus the approximate composition of the alloy No. 23 is:

	Per Cent.
$Fe_3C \cdot U_2C_3$	65
Pearlite	30
FeSi	5·8
V_2C	1·45
Graphite	0·10
	102·35

In the alloys of the second group (Nos. 22 and 25) the main constituent is carbide UC. In No. 25 especially carbide alpha is found as abundantly embedded not only in a separate form (Fig. 1), but also in a fine mixture with ferrite. The mixture [alpha + Fe] has a eutectic appearance; it would likewise seem to replace pearlite absent from these alloys. The author believes this to be a real eutectic.

A portion of the carbon in both alloys enters into combination with vanadium.

Both alloys have a comparatively moderate proportion of carbon, and for this reason they have also the structure of an intermediate type, containing some elements of the structure of low carbon series and some of the high carbon series.

The third group consists of those alloys containing structurally free cementite. Alloy No. 31 contains 4·1 per cent. of uranium. It has the usual structure of the white cast iron, and the uranium in this alloy is present only in the form of the small inclusions of Fe_6U and UC. Alloy No. 28 has a structure composed of Fe_6U, cementite, and pearlite. Only a minute part of uranium forms carbide alpha, the bulk of it being combined with iron in Fe_6U. The latter constituent appears in a fine eutectic-like mixture with cementite (Fig. 16). Fe_3C and Fe_6U are both white, but heat-tinting changes Fe_6U into brown, leaving Fe_3C white, thus producing a differentiation between both constituents. After etching with aqua regia Fe_6U acquires etching pits.

Conclusions.

The observations of the microstructure of ferro-uranium alloys permit us to deduce the following conclusions:

1. Uranium may be present in these alloys as :

   (*a*) Metallic uranium (gamma).
   (*b*) Carbide UC (alpha).
   (*c*) Double carbide $Fe_3C . U_2C_3$ (iota).
   (*d*) Carbide U_2C_3.
   (*e*) Double carbide of alpha and iota.
   (*f*) Fe_6U (beta).
   (*g*) Oxide of U (U_3O_8).

There were likewise found three conglomerates composed of finely divided alternate masses of two constituents and similar to eutectic, namely :

[Gamma + ferrite]
[UC + ferrite]
[Fe_6U + Fe_3C]

2. Constituents containing no uranium in these alloys are as follows : ferrite, pearlite, vanadium carbide (V_2C), silicide (FeSi), graphite.

3. The principal types of microstructure are :

TABLE V.

Main Components.	Chemical Composition of Alloys.	
	Uranium per Cent.	Carbon per Cent.
I. Fe_6U + met. uranium + ferrite	54–39	0·18–1·13
II. Fe_6U + UC + ferrite	31–28	0·34–0·83
III. Ferrite + UC	20	1·10
IV. Ferrite + Fe_6U	17–5	0·53–0·76
V. Ferrite + pearlite + UC (steels) . .	7–0·20	0·20–0·50
VI. $Fe_3C . U_2C_3$ + pearlite + FeSi . .	45–33	4·30–5·0
VII. $Fe_3C . U_2C_3$ + Fe_6U + FeSi . . .	64–48	4·90–6·1
VIII. UC + $Fe_3C . U_2C_3$ + Fe_6U + ferrite . .	46–41	2·30–3·50
IX. Fe_6U + Fe_3C + pearlite	17–4	3·0 –4·3

4. Neither uranium nor any of its above-mentioned compounds forms any solid solution with iron. Uranium carbide UC in steel does not enter into solution with iron even at a temperature as high as 1200°–1250° C.

5. Vanadium possesses greater affinity for carbon than does uranium (alloy No. 12 and others).

The original paper was accompanied by fifty-one micrographs, of which sixteen are reproduced herewith. The remainder are filed in the Library of the Institute and may be consulted by anyone interested. The following is the description of those that have been reproduced on Plates VII. and VIII.:

Fig. 1. Carbide alpha and [alpha + Fe]. Etched with tincture of iodine. × 800 dia.
,, 2. Alpha (UC) and beta (Fe_6U). Heat-tinted. × 1000 dia.
,, 3. Plate-crystals of carbide iota ($Fe_3C . U_2C_3$). Heat-tinted. × 100 dia.
,, 4. Double carbide delta. Etched with picric acid. × 1000 dia.
,, 5. Dark spots represent V_2C. Etched with picric acid. × 165 dia.
,, 6. Metallic uranium (gamma) and eutectic [alpha + Fe]. Heat-tinted and slightly repolished. × 1000 dia.
,, 7. Alloy No. 1. Etched with picric acid. × 275 dia.
,, 8. Alloy No. 1. Heat-tinted. × 100 dia.
,, 9. Alloy No. 10. Heat-tinted and slightly repolished. × 600 dia.
,, 10. Steel No. 16, quenched in water at 1250° C. Heat-tinted and slightly repolished. × 165 dia.
,, 11. Alloy No. 23. Radiograph.
,, 12. Alloy No. 23. Etched with picric acid. × 24 dia.
,, 13. Alloy No. 23. Radiograph. × 24 dia.
,, 14. Alloy No. 23. Etched with picric acid. × 100 dia.
,, 15. [Fe + beta] Fe_6U. Rich in graphite. Heat-tinted and slightly repolished. × 165 dia.
,, 16. Alloy No. 28. Eutectic [Fe_6U + Fe_3C]. Heat-tinted. × 500 dia.

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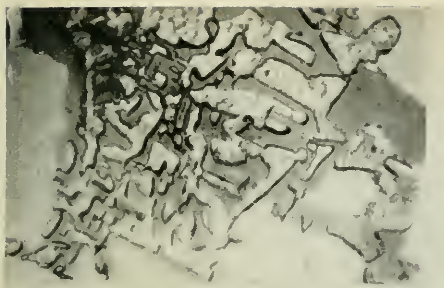
PLATE VII.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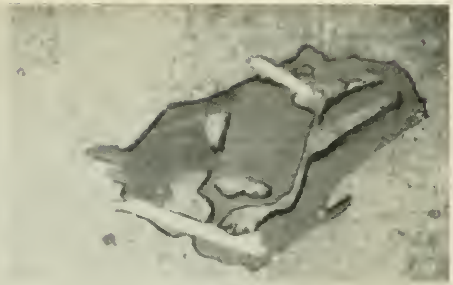
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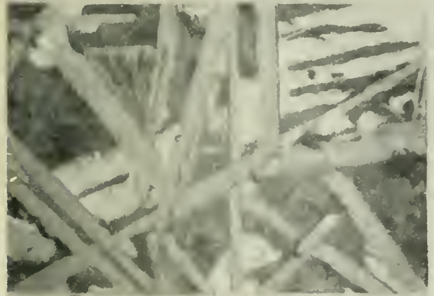
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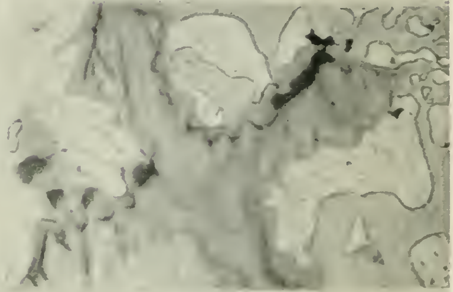
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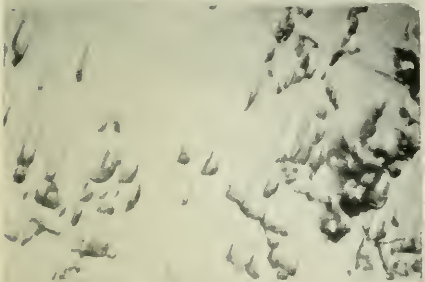
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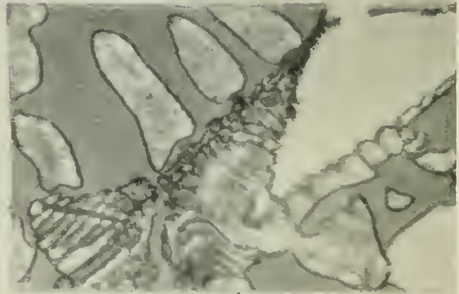
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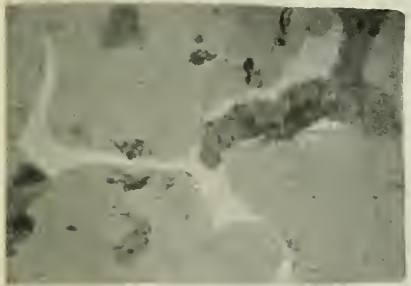
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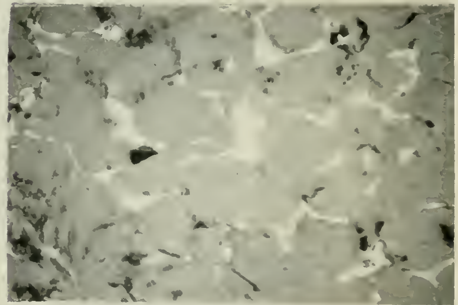
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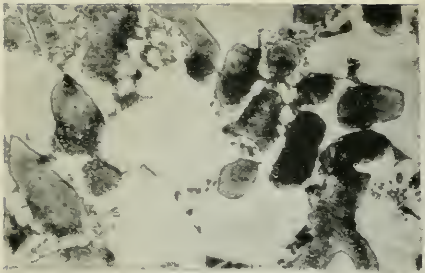
PLATE VIII.



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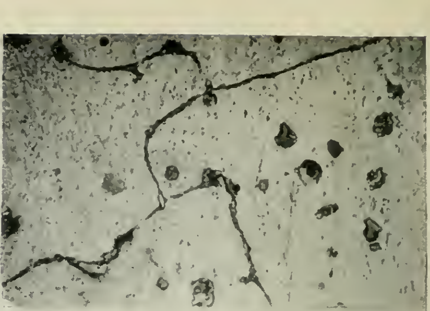

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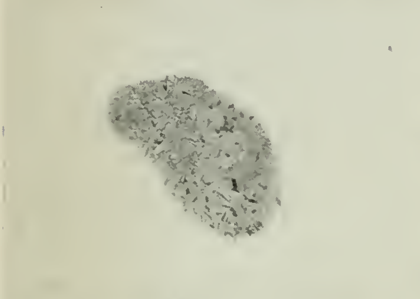

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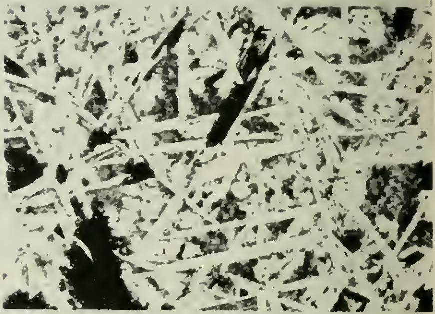

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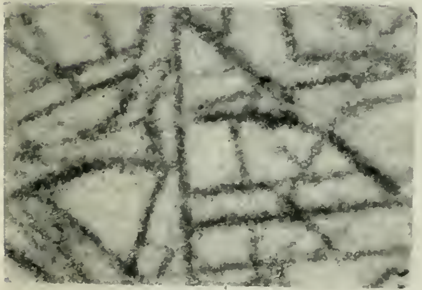

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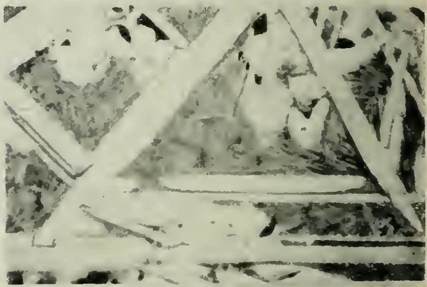

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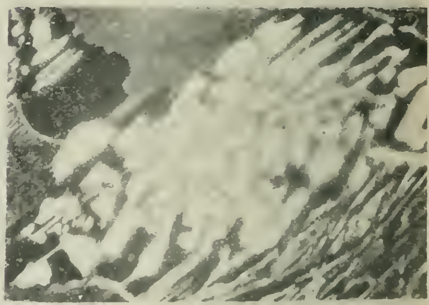

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